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LXXXVII.—GENERALIZATIONS ON DOUBLE HALOGEN SALTS.

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The object of this communication is to point out some conclusions in regard to double halides in general. For this purpose a rather full list of these compounds has been prepared. This list is not supposed to be complete, for the literature has not been searched with care except in the cases of certain series which have been studied in this laboratory,[1] but it is believed to be sufficiently complete for the purpose in view. Care has been taken to consult the original articles where salts of unusual composition have been described, and a few of these have been discarded on account of evidence that they were not real compounds, but no double salt has been rejected simply because it appeared to be irregular.

It has been thought best to limit the present discussion to the salts of the alkali metals, ammonium, and univalent thallium; for, to include the double halides of the organic bases and those in which bivalent metals form the more positive halides, would greatly enlarge the list, probably without giving any additional insight into the nature of the compounds.

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[1] See Am. J. Sci. from 1892 to the present time. References are given beyond to most of these articles, but reference to general literature is not attempted.

For convenience, the double salts will be arranged according to types, which will be designated by ratios indicating the number of atoms of the two metals; thus, $KCl.SnCl_2$ is a 1 : 1 salt; $2KCl.PtCl_4$ is a 2 : 1 salt; and $CsCl.2PbCl_2$ is a 1 : 2 salt. The number referring to the atoms of alkali metal, etc., will be invariably placed first.

I. SALTS OF UNIVALENT NEGATIVE METALS.

Cuprous Salts.[1]

3 : 1	2 : 1	3 : 2
$3CsCl.CuCl.H_2O$	$2NH_4Cl.CuCl$	$3CsCl.2CuCl$
	$2NH_4Br.CuBr$	
	$2KCl.CuCl$	

1 : 1	2 : 3	1 : 2
$NH_4Cl.CuCl$	$2NH_4Cl.3CuCl$	$CsCl.2CuCl$
$NH_4Br.CuBr$		
$NH_4I.CuI.H_2O$.		

Silver and Aurous Salts.[2]

2 : 1	1 : 1
$2KI.AgI$	$NH_4Cl.AgCl$
$2RbI.AgI$	$KCl.AgCl$
$2CsI.AgI$	$KI.AgI$
	$KCl.AuCl$

II. SALTS OF BIVALENT NEGATIVE METALS.

Beryllium Salts.

2 : 1	1 : 1
$2KF.BeF_2$	$KF.BeF_2$
$2KCl.BeCl_2$	

Magnesium Salts.[3]

1 : 1	
$NH_4Cl.MgCl_2.6H_2O$	$KCl.MgCl_2.6H_2O$
$NH_4Br.MgBr_2.6H_2O$	$KBr.MgBr_2.6H_2O$
$NH_4I.MgI_2.6H_2O$	$KI.MgI_2.6H_2O$
$NaF.MgF_2$	$RbCl.MgCl_2.6H_2O$
$NaCl.MgCl_2.H_2O$	$CoCl.MgCl_2.6H_2O$
	$CsBr.MgBr_2.6H_2O$

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[1] Am. J. Sci., (3), **47**, 96.

[2] *Ibid.*, (3), **44**, 155, 157.

[3] Wells and Campbell: *Ibid.*, (3), **46**, 431.

Manganese Salts.[1]

2 : 1	1 : 1
$2NH_4Cl.MnCl_2.2H_2O$	$NH_4Cl.MnCl_2.2H_2O$
$2RbCl.MnCl_2.2H_2O$	$KCl.MnCl_2.2H_2O$
$2CsCl.MnCl_2.2H_2O$	$CsCl.MnCl_2.2H_2O$

Ferrous and Nickel Salts.

2 : 1	1 : 1
$2NH_4Cl.FeCl_2$	$KF.FeF_2.H_2O$
$2KF.FeF_2$	$NH_4Cl.NiCl_2.6H_2O$
$2KCl.FeCl_2.2H_2O$	$NaF.NiF_2.H_2O$
$2NH_4F.NiF_2.2H_2O$	$KF.NiF_2.H_2O$
$2KF.NiF_2$	$CsCl.NiCl_2$
	$CsBr.NiBr_2$

Cobalt Salts.[2]

3 : 1	2 : 1	1 : 1
$3CsCl.CoCl_2$	$2NH_4F.CoF_2.2H_2O$	$NH_4Cl.CoCl_2.6H_2O$
$3CsBr.CoBr_2$	$2CsCl.CoCl_2$	$NaF.CoF_2.H_2O$
	$2CsBr.CoBr_2$	$KF.CoF_2.H_2O$
	$2CsI.CoI_2$	$CsCl.CoCl_2.2H_2O$

Cupric Salts.[3]

2 : 1	3 : 2
$2NH_4F.CuF_2.2H_2O$	$3CsCl.2CuCl_2.2H_2O$
$2NH_4Cl.CuCl_2.2H_2O$	
$2NH_4Br.CuBr_2.2H_2O$	
$2KF.CuF_2$	
$2KCl.CuCl_2$	
$2CsCl.CuCl_2$	
$2CsCl.CuCl_2.2H_2O$	
$2CsBr.CuBr_2$	

1 : 1	
$NH_4F.CuF_2.2\frac{1}{2}H_2O$	$RbF.CuF_2$
$NH_4Cl.CuCl_2.2H_2O$	$CsCl.CuCl_2$
$LiCl.CuCl_2.2H_2O$	$CsBr.CuBr_2$
$KF.CuF_2$	

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[1] Saunders: This JOURNAL, **14**, 152.

[2] Campbell: Am. J. Sci., (3), **48**, 418.

[3] Wells and Dupee: *Ibid.*, (3), **47**, 91.

Zinc Salts.[1]

4 : 1

$4NH_4Cl.ZnCl_2$

3 : 1

$3NH_4Cl.ZnCl_2$
$3CsCl.ZnCl_2$
$3CsBr.ZnBr_2$
$3CsI.ZnI_2$

2 : 1

$2NH_4F.ZnF_2.2H_2O$
$2NH_4Cl.ZnCl_2$
$2NH_4Cl.ZnCl_2.H_2O$
$2NH_4Br.ZnBr_2$
$2NH_4I.ZnI_2$
$2NaCl.ZnCl_2.3H_2O$
$2NaI.ZnI_2.3H_2O$
$2KF.ZnF_2$
$2KCl.ZnCl_2$
$2KI.ZnI_2$
$2CsCl.ZnCl_2$
$2CsBr.ZnBr_2$
$2CsI.ZnI_2$

1 : 1

$NH_4Cl.ZnCl_2.2H_2O$
$NaF.ZnF_2$
$NaI.ZnI_2.3H_2O$
$KF.ZnF_2$
$KI.ZnI_2$

Cadmium Salts.[2]

4 : 1

$4NH_4Cl.CdCl_2$
$4NH_4Br.CdBr_2$
$4KCl.CdCl_2$
$4KBr.CdBr_2$

3 : 1

$3CsBr.CdBr_2$
$3CsI.CdI_2$

2 : 1

$2NH_4Cl.CdCl_2$
$2NH_4Cl.CdCl_2.H_2O$
$2NH_4Br.CdBr_2.\frac{1}{2}H_2O$
$2NH_4I.CdI_2.2H_2O$
$2NaCl.CdCl_2.3H_2O$
$2NaBr.CdBr_2.5H_2O$
$2NaI.CdI_2.6H_2O$
$2KCl.CdCl_2$
$2KCl.CdCl_2.H_2O$
$2KBr.CdBr_2$
$2KI.CdI_2.2H_2O$
$2CsCl.CdCl_2$
$2CsBr.CdBr_2$
$2CsI.CdI_2$

1 : 1

$NH_4F.CdF_2$
$NH_4Br.CdBr_2.\frac{1}{2}H_2O$
$NaBr.CdBr_2.2\frac{1}{2}H_2O$
$KCl.CdCl_2$
$KCl.CdCl_2.\frac{1}{2}H_2O$
$KBr.CdBr_2.\frac{1}{2}H_2O$
$KI.CdI_2.H_2O$
$CsCl.CdCl_2$
$CsBr.CdBr_2$
$CsI.CdI_2$

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[1] Wells and Campbell : Am. J. Sci., (3), **46**, 431.

[2] Wells and Walden : *Ibid.*, (3), **46**, 425.

Stannous Salts.

4 : 1

$4NH_4Cl.SnCl_2.3H_2O$

$4KCl.SnCl_2.3H_2O$

2 : 1

$2NH_4F.SnF_2.2H_2O$

$2NH_4Cl.SnCl_2.H_2O$

1 : 1

$NH_4I.SnI_2$

$NH_4I.SnI_2.1\frac{1}{2}H_2O$

$NaI.SnI_2$

$KI.SnI_2.1\frac{1}{2}H_2O$

2 : 3

$2NaF.3SnF_2$

$2KF.3SnF_2.H_2O$

Mercuric Salts.[1]

3 : 1

$3CsCl.HgCl_2$

$3CsBr.HgBr_2$

$3CsI.HgI_2$

2 : 1

$2NH_4Cl.HgCl_2.H_2O$

$2NH_4Br.HgBr_2$

$2NH_4I.HgI_2.3H_2O$

$2NaCl.HgCl_2$

$2NaI.HgI_2$

$2KCl.HgCl_2.H_2O$

$2KBr.HgBr_2$

$2KI.HgI_2$

$2RbCl.HgCl_2$

$2RbCl.HgCl_2.2H_2O$

$2CsCl.HgCl_2$

$2CsBr.HgBr_2$

$2CsI.HgI_2$

1 : 1

$NH_4Cl.HgCl_2$

$NH_4Cl.HgCl_2.H_2O$

$NH_4Br.HgBr_2$

$NH_4I.HgI_2.H_2O$

$LiCl.HgCl_2$

$NaCl.HgCl_2.1\frac{1}{2}H_2O$

$NaBr.HgBr_2$

$NaI.HgI_2.1\frac{1}{2}H_2O$

$KCl.HgCl_2$

$KCl.HgCl_2.H_2O$

$KBr.HgBr_2$

$KBr.HgBr_2.H_2O$

$KI.HgI_2.1\frac{1}{2}H_2O$

$RbCl.HgCl_2$

$CsCl.HgCl_2$

$CsBr.HgBr_2$

$CsI.HgI_2$

$TlCl.HgCl_2$

2 : 3

$2NH_4Cl.3HgCl_2.4H_2O$

$2CsI.3HgI_2$

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[1] Am. J. Sci., (3), 44, 221.

1 : 2

$KCl.2HgCl_2.2H_2O$
$RbCl.2HgCl_2$
$CsCl.2HgCl_2$
$CsBr.2HgBr_2$
$CsI.2HgI_2$

1 : 5

$NH_4Cl.5HgCl_2$
$CsCl.5HgCl_2$

Palladious, Platinous, and Iridious Salts.

2 : 1

$2NH_4Cl.PdCl_2$
$2NH_4Cl.PtCl_2$
$2NH_4I.IrI_2$
$2NaCl.PdCl_2$
$2NaCl.PtCl_2.4H_2O$
$2KCl.PdCl_2$
$2KCl.PtCl_2$
$2KBr.PtBr_2$
$2CsCl.PdCl_2$
$2CsCl.PtCl_2$

1 : 1

$LiCl.PtCl_2.6H_2O$
$KCl.PdCl_2$
$KCl.PtCl_2$
$RbCl.PtCl_2$

Lead Salts.[1]

4 : 1

$4CsCl.PbCl_2$
$4CsBr.PbBr_2$

2 : 1

$2NH_4Br.PbBr_2.H_2O$
$2KBr.PbBr_2.H_2O$
$2RbCl.PbCl_2.\frac{1}{2}H_2O$
$2RbBr.PbBr_2.\frac{1}{2}H_2O$

1 : 1

$NH_4Cl.PbCl_2.\frac{1}{3}H_2O$
$NH_4I.PbI_2.2H_2O$
$KCl.PbCl_2.\frac{1}{3}H_2O$
$KBr.PbBr_2.\frac{1}{3}H_2O$
$KBr.PbBr_2.H_2O$
$KI.PbI_2.2H_2O$
$RbI.PbI_2.2H_2O$
$CsCl.PbCl_2$
$CsBr.PbBr_2$
$CsI.PbI_2$

1 : 2

$NH_4Cl.2PbCl_2$
$NH_4Br.2PbBr_2$
$KCl.2PbCl_2$
$KBr.2PbBr_2$
$RbCl.2PbCl_2$
$RbBr.2PbBr_2$
$CsCl.2PbCl_2$
$CsBr.2PbBr_2$

III. SALTS OF TRIVALENT NEGATIVE METALS.

Aluminium Salts.

3 : 1

$3NH_4F.AlF_3$
$3NaF.AlF_3$
$3KF.AlF_3$

2 : 1

$2NaF.AlF_3$
$2KF.AlF_3$

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[1] Nearly all the older work on double halides of lead was entirely erroneous. See Remsen and Herty: This JOURNAL, 14, 107; Wells: Am. J. Sci., (3), 45, 121; Wells and Johnson: *Ibid.*, 46, 25, 34.

3 : 2

$3NaF.2AlF_3$[1]

1 : 1

$NaCl.AlCl_3$
$KCl.AlCl_3$
$KBr.AlBr_3$
$KI.AlI_3$

Vanadium Salts.

3 : 1

$3NH_4F.VF_3$

5 : 2

$5NaF.2VF_3.H_2O$

2 : 1

$2NH_4F.VF_3.H_2O$
$2KF.VF_3.H_2O$

1 : 1

$NH_4F.VF_3.2H_2O$

Chromium Salts.[2]

3 : 1

$3NH_4F.CrF_3$
$3KF.CrF_3$
$3KCl.CrCl_3$
$3TlCl.CrCl_3$

2 : 1

$2NH_4F.CrF_3.H_2O$
$2NH_4Cl.CrCl_3.H_2O$
$2NaF.CrF_3.H_2O$
$2KF.CrF_3.H_2O$
$2KCl.CrCl_3.2H_2O$
$2CsCl.CrCl_3.H_2O$
$2CsCl.CrCl_3.4H_2O$

1 : 1

$KCl.CrCl_3$

Titanous and Manganic Salts.

3 : 1

$3NH_4F.TiF_3$

2 : 1

$2NH_4F.MnF_3$
$2NaF.MnF_3$
$2KF.MnF_3$
$2NH_4F.TiF_3$

Ferric Salts.[3]

3 : 1

$3NH_4F.FeF_3$
$3KF.FeF_3$
$3CsCl.FeCl_3.H_2O$
$3TlCl.FeCl_3$.

2 : 1

$2NH_4F.FeF_3$
$2NH_4Cl.FeCl_3$
$2NaF.FeF_3.\frac{1}{2}H_2O$
$2NaCl.FeCl_3.H_2O$
$2KF.FeF_3$
$2KCl.FeCl_3.H_2O$
$2RbCl.FeCl_3.H_2O$
$2RbBr.FeBr_3.H_2O$
$2CsCl.FeCl_3.H_2O$
$2CsBr.FeBr_3.H_2O$

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[1] The formula for chiolite is somewhat doubtful. Some authorities prefer the formula $5NaF.3AlF_3$, but the simpler formula is selected here.

[2] Wells and Boltwood: Am. J. Sci., (3), 50, 249.

[3] Walden: *Ibid.*, (3), 48, 283.

1 : 1

$NH_4Br.FeBr_3.2H_2O$
$CsCl.FeCl_3$
$CsBr.FeBr_3$

Arsenious Salts.[1]

3 : 2

$3RbCl.2AsCl_3$
$3RbBr.2AsBr_3$
$3RbI.2AsI_3$

$3CsCl.2AsCl_3$
$3CsBr.2AsBr_3$
$3CsI.2AsI_3$

Indium Salts.

3 : 1

$3KCl.InCl_3.1\frac{1}{2}H_2O$

2 : 1

$2NH_4Cl.InCl_3.H_2O$

Antimonious Salts.[2]

4 : 1

$4NH_4I.SbI_3.3H_2O$

3 : 1

$3NH_4Cl.SbCl_3.1\frac{1}{2}H_2O$
$3NaF.SbF_3$
$3NaCl.SbCl_3$

7 : 3

$7KCl.3SbCl_3$
$7KBr.3SbBr_3.8H_2O$
$7RbCl.3SbCl_3$
$7RbBr.3SbBr_3$

2 : 1

$2NH_4F.SbF_3$
$2NH_4Cl.SbCl_3$
$2NH_4Cl.SbCl_3.H_2O$
$2LiF.SbF_3$
$2KF.SbF_3$
$2KCl.SbCl_3$
$2KCl.SbCl_3.2H_2O$
$2CsF.SbF_3$

3 : 2

$3NH_4I.2SbI_3.3H_2O$
$3NaI.2SbI_3.12H_2O$
$3KI.2SbI_3.3H_2O$
$3RbCl.2SbCl_3$
$3RbBr.2SbBr_3$
$3RbI.2SbI_3$
$3CsCl.2SbCl_3$
$3CsI.2SbI_3$

1 : 1

$NH_4Cl.SbCl_3$
$NH_4I.SbI_3.2H_2O$
$KF.SbF_3$
$KI.SbI_3.H_2O$
$RbCl.SbCl_3$
$CsF.SbF_3$

3 : 4

$3NH_4I.4SbI_3.9H_2O$

4 : 7

$4CsF.7SbF_3$

1 : 2

$RbCl.2SbCl_3$
$CsF.2SbF_3$

1 : 3

$CsF.3SbF_3$

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[1] **Wheeler : Am. J. Sci., (3), 46, 88.**

[2] **Wheeler : *Ibid.*, (3), 46, 269 ; Wells and Metzger : *Ibid.*, (4), 11, 451.**

Auric Salts.[1]

1 : 1

$NH_4Cl.AuCl_3.H_2O$
$NH_4Cl.AuCl_3.2\frac{1}{2}H_2O$
$NaCl.AuCl_3.2H_2O$
$NaBr.AuBr_3.2H_2O$
$KCl.AuCl_3.\frac{1}{2}H_2O$
$KCl.AuCl_3.2H_2O$
$KBr.AuBr_3.2H_2O$
$KI.AuI_3$
$RbCl.AuCl_3$
$RbBr.AuBr_3$
$CsCl.AuCl_3$
$CsCl.AuCl_3.\frac{1}{2}H_2O$
$CsBr.AuBr_3$
$TlCl.AuCl_3$

Rhodium, Ruthenium, Indium, and Osmium Salts.

3 : 1

$3NH_4Cl.RhCl_3.1\frac{1}{2}H_2O$
$3NH_4Cl.IrCl_3.1\frac{1}{2}H_2O$
$3NH_4Br.IrBr_3.\frac{1}{2}H_2O$
$3NH_4I.IrI_3.\frac{1}{2}H_2O$
$3NaCl.RhCl_3.9H_2O$
$3NaCl.IrCl_3.12H_2O$
$3NaBr.IrBr_3.\frac{1}{2}H_2O$
$3KCl.RhCl_3$
$3KCl.IrCl_3.3H_2O$
$3KBr.IrBr_3.3H_2O$
$3KI.IrI_3$
$3KCl.OsCl_3.6H_2O$

2 : 1

$2NH_4Cl.RhCl_3.H_2O$
$2NH_4Cl.RuCl_3$
$2NH_4Cl.OsCl_3.1\frac{1}{2}H_2O$
$2KCl.RhCl_3.H_2O$
$2KCl.RhCl_3.3H_2O$
$2KCl.RuCl_3$

Bismuth Salts.

4 : 1

$4NH_4Cl.BiCl_3$
$4KI.BiI_3$

3 : 1

$3NH_4Cl.BiCl_3$
$3NaCl.BiCl_3$
$3KCl.BiCl_3$
$3KI.BiCl_3$
$3RbCl.BiCl_3$
$3CsCl.BiCl_3$

7 : 3

$7RbCl.3BiCl_3$

2 : 1

$2NH_4Cl.BiCl_3$
$2NaCl.BiCl_3.3H_2O$
$2KCl.BiCl_3.2H_2O$
$2KI.BiI_3.H_2O$

3 : 2

$3NaI.2BiI_3$
$3KCl.2BiCl_3$
$3CsCl.2BiCl_3$

1 : 1

$NH_4Cl.BiCl_3$
$KCl.BiCl_3.H_2O$
$KI.BiI_3$
$RbCl.BiCl_3.H_2O$

1 : 2

$NH_4Cl.2BiCl_3$

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[1] Wells and Wheeler: Am. J. Sci., (3), **44**, 157.

Thallic Salts.[1]

5 : 1

$5TlI.TlI_3$

3 : 1

$3NH_4Cl.TlCl_3.2H_2O$
$3NH_4Cl.TlCl_3$
$3NH_4I.TlI_3$
$3LiCl.TlCl_3.8H_2O$
$3NaCl.TlCl_3.12H_2O$
$3KCl.TlCl_3.2H_2O$
$3RbCl.TlCl_3.H_2O$
$3RbBr.TlBr_3.H_2O$
$3CsCl.TlCl_3.H_2O$
$3TlCl.TlCl_3$
$3TlBr.TlBr_3$

2 : 1

$2KCl.TlCl_3.2H_2O$
$2RbCl.TlCl_3.H_2O$
$2CsCl.TlCl_3$
$2CsCl.TlCl_3.H_2O$

3 : 2

$3KCl.2TlCl_3.1\frac{1}{2}H_2O$
$3KBr.2TlBr_3.3H_2O$
$3KI.TlI_3.3H_2O$
$3CsCl.2TlCl_3$
$3CsBr.2TlBr_3$

1 : 1

$NH_4Br.TlBr_3.2H_2O$
$NH_4Br.TlBr_3.4H_2O$
$NH_4Br.TlBr_3$
$NH_4I.TlI_3$
$KBr.TlBr_3$
$KI.TlI_3$
$RbBr.TlBr_3$
$RbI.TlI_3$
$CsBr.TlBr_3$
$CsI.TlI_3$
$TlCl.TlCl_3$
$TlBr.TlBr_3$

IV. SALTS OF QUADRIVALENT NEGATIVE METALS.

Titanic,[2] *Germanium, and Manganese Salts.*

2 : 1

$2NH_4F.TiF_4$
$2NaF.TiF_4$
$2KF.TiF_4.H_2O$
$2RbF.TiF_4$
$2KF.MnF_4$
$2KF.GeF_4$

Zirconium Salts.[3]

4 : 1

$4LiF.ZrF_4.\frac{2}{3}H_2O$

3 : 1

$3NH_4F.ZrF_4$
$3KF.ZrF_4$

5 : 2

$5NaF.2ZrF_4$

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[1] Pratt : Am. J. Sci., (3), 49, 397.

[2] Rose's compounds, $6NH_4Cl.TiCl_4$ and $3NH_4Cl.TiCl_4$, are omitted here because they represent sublimates of variable composition. Pennington's salt, $4CsF.TiF_4$, is also left out, as it was described with two other caesium salts of very suspicious composition, which are referred to under the pentavalent compounds.

[3] Wells and Foote : *Ibid.*, (4), 1, 18 ; 3, 466.

2 : 1

$2NH_4F.ZrF_4$
$2LiF.ZrF_4$
$2NaF.ZrF_4$
$2NaCl.ZrCl_4$
$2KF.ZrF_4$
$2CsF.ZrF_4$

5 : 3

$5TlF.3ZrF_4$

1 : 1

$KF.ZrF_4.H_2O$
$CsF.ZrF_4$
$TlF.ZrF_4$
$TlF.ZrF_4.H_2O$

2 : 3

$2CsF.3ZrF_4.2H_2O$

Stannic and Antimony Salts.

4 : 1

$4NH_4F.SnF_4$

2 : 1

$2NH_4Cl.SnCl_4$
$2LiF.SnF_4.2H_2O$
$2NaF.SnF_4$
$2NaCl.SnCl_4$
$2NaCl.SnCl_4.6H_2O$
$2NaBr.SnBr_4.6H_2O$

$2KF.SnF_4.H_2O$
$2KCl.SnCl_4$
$2RbCl.SnCl_4$
$2CsCl.SnCl_4$
$2CsCl.SbCl_4$

Tellurium Salts.[1]

2 : 1

$2KCl.TeCl_4$
$2KBr.TeBr_4.2H_2O$
$2KI.TeI_4.2H_2O$
$2RbCl.TeCl_4$
$2RbBr.TeBr_4$

$2RbI.TeI_4$
$2CsCl.TeCl_4$
$2CsBr.TeBr_4$
$2CsI.TeI_4$

1 : 1

$NH_4F.TeF_4$
$KF.TeF_4$
$CsF.TeF_4$

Ceric Salt.

3 : 2

$3KF.CeF_4.2H_2O$

Platinum Group Salts.

2 : 1

$2NH_4Cl.PdCl_4$
$2NH_4Cl.RuCl_4$
$2NH_4Cl.IrCl_4$
$2NH_4Cl.PtCl_4$
$2NH_4Cl.OsCl_4$
$2NH_4Br.PtBr_4$
$2NH_4Br.IrBr_4$
$2NH_4I.PtI_4$
$2LiCl.PtCl_4.6H_2O$
$2NaCl.PtCl_4.6H_2O$

$2NaCl.IrCl_4.6H_2O$
$2NaCl.OsCl_4$
$2NaBr.IrBr_4$
$2NaI.PtI_4.6H_2O$
$2NaI.IrI_4$
$2KCl.PdCl_4$
$2KCl.RuCl_4$
$2KCl.PtCl_4$
$2KCl.IrCl_4$

$2KCl.OsCl_4$
$2KBr.PdBr_4$
$2KBr.PtBr_4$
$2KBr.IrBr_4$
$2KI.PtI_4$
$2KI.IrI_4$
$2RbCl.PtCl_4$
$2CsCl.PtCl_4$
$2TlCl.PtCl_4$

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[1] Wheeler : Am. J. Sci., (3), 45, 267.

Plumbic Salts.[1]

2 : 1	
$2NH_4Cl.PbCl_4$	$2RbCl.PbCl_4$
$2KCl.PbCl_4$	$2CsCl.PbCl_4$

Thorium Salts.[2]

3 : 1	2 : 1
$3CsCl.ThCl_4.12H_2O$	$2KF.ThF_4.4H_2O$
	$2CsCl.ThCl_4.11H_2O$

1 : 1	1 : 2
$KF.ThF_4.\frac{1}{2}H_2O$	$KCl.2ThCl_4.18H_2O$

V. SALTS OF QUINQUIVALENT NEGATIVE METALS.[3]

4 : 1	2 : 1	1 : 1
$4NH_4Cl.SbCl_4$	$2KF.AsF_5$	$KF.AsF_5$
	$2NH_4F.SbF_5$	$NH_4F.SbF_5$
	$2KF.SbF_5$	$NaF.SbF_5$
	$2KF.NbF_5$	$KF.SbF_5$
	$2RbF.NbF_5$	
	$2NH_4F.TaF_5$	
	$2NaF.TaF_5$	
	$2KF.TaF_5$	
	$2RbF.TaF_5$	

Upon examining this table a marked similarity is to be noticed in the different series ; the 2 : 1 and 1 : 1 types are common to all ; the 4 : 1, 3 : 1, 3 : 2, and 1 : 2 types are found in all but one ; while 2 : 3 types are found in three of the series. Besides the seven types just mentioned there are eight others, but only one of the latter exists in more than one series, and most of them are represented by only a single salt. It is quite possible that some of these unusual ratios are due to erroneous descriptions of salts, but it is certain that many of them represent real compounds.

The remarkable similarity in the prominent types of the

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[1] Am. J. Sci., (3), **46**, 180.

[2] The salt $8NH_4Cl.ThCl_4.8H_2O$, described by Chydenius as a sintered mass, is rejected, as is also $8KF.7ThF_4.6H_2O$, which Chydenius himself considered to be probably a mixture.

[3] Pennington's salts, $7CsF.NbF_5$ and $15CsF.TaF_5$, are omitted because they differ entirely from two rubidium salts obtained in the same investigation (which are given in the list), and because they depend upon single partial analyses (see J. Am. Chem. Soc., **18**, 59). It is impossible to believe that caesium and rubidium salts of the same metals should differ so widely as these appear to do.

Types Arranged According to the Valency of the Negative Metals.

In this table the number of salts given in the preceding lists is placed under each type :

Valency.																Total
I	....	....	3 : 1 1	....	....	2 : 1 6	3 : 2 1	....	1 : 1 7	....	2 : 3 1	....	1 : 2 1	....	....	17
II	....	4 : 1 9	3 : 1 11	....	....	2 : 1 78	3 : 2 1	....	1 : 1 83	....	2 : 3 4	....	1 : 2 13	....	1 : 5 2	201
III	5 : 1 1	4 : 1 3	3 : 1 46	5 : 2 1	7 : 3 5	2 : 1 48	3 : 2 23	....	1 : 1 45	3 : 4 1	....	4 : 7 1	1 : 2 3	1 : 3 1	....	178
IV	....	4 : 1 2	3 : 1 3	5 : 2 1	....	2 : 1 66	3 : 2 1	5 : 3 1	1 : 1 8	....	2 : 3 1	....	1 : 2 1	....	....	84
V	....	4 : 1 1	....	....	....	2 : 1 9	....	....	1 : 1 4	....	....	....	....	....	....	14
Total	5 : 1 1	4 : 1 15	3 : 1 61	5 : 2 2	7 : 3 5	2 : 1 207	3 : 2 26	5 : 3 1	1 : 1 147	3 : 4 1	2 : 3 6	4 : 7 1	1 : 2 18	1 : 3 1	1 : 5 2	494

series of different valencies leads to the conclusion that *the valency of a negative halide has no influence upon the types of double salts that it forms.* For, if valency had an influence it would be expected that the five series would show marked differences from one another, and probably the halides of higher valency would tend to combine with a larger number of alkaline halide molecules. Instead of a progression of types as valency increases, however, the table shows a marked symmetry in types, and their arithmetical limits in both directions are as nearly constant as could be expected, considering the variations in the numbers of known salts in the different series. The prominence of the 3 : 1 and 3 : 2 types in the trivalent series may perhaps be taken as an indication that the rule is not absolute, but since these types are not the only prominent ones, and since both of them occur in three other series, the circumstance that many are found in the trivalent series may be accidental.

The facts, mentioned above, that the ratios of the different series are nearly symmetrical and that the arithmetical limits of the types in *both directions* are nearly uniform appear to be important, for they indicate that the ratios according to which positive and negative halides combine are not influenced to any great degree by the positive or negative nature of the halides. In other words, *the molecules of alkaline halides possess nearly the same combining power as molecules of negative halides.* Perhaps this point may be made clearer by the statement that if all the ratios in the table are read backward they remain almost unchanged in their arithmetical aspect, and in the cases of most of the prominent ratios there is actually no change; for instance, the list of ratios 5 : 1, 3 : 1, 2 : 1, 3 : 2, 1 : 1, 2 : 3, 1 : 2, 1 : 3, and 1 : 5 is the same whether read forward or backward, and to these ratios belong almost 95 per cent of the salts here considered. It is evident, however, that positive and negative halides are not of *exactly* equal numerical importance, for to the left of the 1 : 1 ratio in the table, toward the positive halide end, the ratios are more numerous and the salts far more abundant than toward the negative halide end; it appears to be the 3 : 2 ratio column that forms a nearly symmetrical dividing line between the positive and negative ends, and even with this division the salts on the positive side predominate in number.

Another point to which attention may be called is that *salts of simple types predominate.* More than 71 per cent of the salts in the list belong to the 2 : 1 and 1 : 1 ratios, while the 4 : 1, 3 : 1, 3 : 2, 2 : 3, and 1 : 2 ratios represent over 25 per cent of them. The remaining eight types, most of which are more complex, include less than 3 per cent of all the salts. The fact that the 2 : 1 and 1 : 1 ratios are so important in *all* the series, is another indication that valency does not influence the ratios according to which halides combine. Another evidence of simplicity is the circumstance, that as far as is known, not more than 5 molecules of one halide can combine with 1 molecule of another in extreme cases, while the usual limit is 2, 3, or 4. It is undoubtedly a fact that there are a few complicated salts which are not derived from mixtures or poor analyses. For example, the antimony salts to which is here given the 7 : 3 ratio have been thoroughly investigated, and, without doubt, possess either this ratio or one still more complex.

The conclusions that have been reached above are not encouraging in the way of giving an insight to the structure of double halides, for, if valency plays no part in this, the number of halogen atoms likewise has no influence, and such laws or rules, based on halogen atoms, as have been advanced must be abandoned. Professor Remsen's law,[1] which states that the number of alkaline halide molecules that can combine with a negative halide molecule is not greater than the valency of the latter, is evidently one of these. The dotted line in the table of ratios shows a region in the upper left-hand corner which is beyond the domain of this law. At the time that the law was brought forward it seemed reasonable, for there were only two or three possible exceptions to it. With our present knowledge of the subject, however, it is evident that it is an accidental circumstance that the law applies to so many double halides, for it is the small number of known double halides of univalent negative metals, as well as the rarity of salts of high alkali-metal ratios in the subsequent series, which determines the comparatively small number of exceptions to this rule. Werner's theory,[1] depending as it does upon definite numbers of halogen and other atoms, appears to have no application to the double halides in general. Possibly it may apply to the salts that form complex ions in solution.

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[1] This JOURNAL, 11, 296; 14, 85.

A prevalent idea concerning the influence of valency in the formation of simple oxygen salts seems to need revision also, for halogen and oxygen salts appear to be governed by the same laws. For instance, there is no good reason for considering the valency of sulphur to have an influence upon the types of sulphates that can exist, and consequently for imagining an ideal or "ortho" sulphate such as K_6SO_6.

As far as double oxygen salts are concerned, there can be little doubt that they are analogous to double halogen salts. Their molecules usually unite in 2 : 1 or 1 : 1 ratios. A double oxygen salt, however, in view of the analogy between double halogen and simple oxygen salts, may be considered as analogous to a double-double halogen salt, if such there be. Possibly some of the complex types of double halogen salts may be due to such combinations; for instance, $2Rb_3SbCl$ (unknown) $+ RbSbCl_4 = 7RbCl.3SbCl_3$.

The stability of double halogen salts when they are dissolved in water varies exceedingly, but since gradations occur, and there is no sharp dividing line between classes of different stability, it cannot be supposed that there is any real difference in structure, as far as the solid state is concerned, between these different classes. In fact, salts that are isomorphous and evidently strictly analogous, vary greatly in their behavior in solution; for example, the octahedral salts K_2PtCl_6, K_2SnCl_6, and K_2PbCl_6.

Although only two classes of double salts, based on their behavior in solution, are usually recognized, there are three more or less distinctly defined groups, the first, of which K_2PtCl_6 is an example, undergoes ionization into alkali-metal ions and complex negative ions, with little or no decomposition into the simple halides. It is this class which displays a striking similarity to simple oxygen salts. They are comparatively few in number, but the double cyanides, which are probably entirely analogous to double halides, furnish many examples of them. The second group consists of salts that readily separate into their component halides in solution, but which may be recrystallized unchanged from water or from dilute acid solutions. To the third class belong salts that require the presence of an excess of one of their halides in solution in order that they may be formed. Sometimes the excess required is very great, so that the proportion of halides in the solution is widely different from that in the salt that crystallizes out. It is by varying the proportions of two halides greatly that a series of several double salts may sometimes be produced from them.

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[1] Ztschr. anorg. Chem., 3, 267.

The fact that the same two halides may unite in several proportions to form different double salts is a point that has been sometimes disregarded by chemists. Some investigators have been content with the preparation of a single compound in cases where several might have been produced. This is a matter that should be borne in mind in the study of the physical properties of solutions. The largest number of double halides that have been produced by combining two simple halides appears to be five; for instance, five caesium mercuric chlorides and five caesium antimonious fluorides are the most extensive series of this kind that are known. Such series appear to be limited by a sort of overlapping of conditions, for compounds that are expected from analogy, intermediate between two that are produced, often cannot be prepared, and where a single double salt is very stable it may be the only one that can be made. Where several double halides of the same two simple halides exist, it is usually the case that one of them is the most stable one and that this is produced by the recrystallization of the others, but cases occur where two of the salts, at least, are unchanged by recrystallizing.

The water of crystallization of double halides appears to present precisely the same problem as in the case of simple salts, for we find double salts of the same type possessing no water and varying quantities of it, and no good evidence is to be found that in these compounds a molecule of water is equivalent to an alkaline halide molecule, a relation similar to that, for example, that has been supposed to exist between the compounds $FeSO_4.7H_2O$ and $FeSO_4.(NH_4)_2SO_4.6H_2O$.

It has been pointed out previously[1] that double halides seem to show an increase in stability and variety from the iodides to the chlorides, and apparently also to the fluorides. It is probable that this is a general rule among these compounds.

It has been shown[2] also that with the metals magnesium, zinc, cadmium, and mercury the tendency to form double halides increases with the atomic weights. This tendency is found in other cases also, but from a comparison of the zirconium and thorium salts, as well as the antimonious and bismuth salts, it seems doubtful that this is a rule that applies in all cases.

It has been found in some cases[3] that caesium appears to form more extensive series of double salts than the other alkali metals, but evidently there are exceptions to this rule, for Wells and Campbell[4] were unable to prepare any caesium magnesium iodide, although both ammonium and potassium magnesium iodides are known.

The rule advanced by Godeffroy[5] that all the double salts of caesium are less soluble than those of the other alkali metals, while true in most instances, is apparently not invariable, for Wells and Campbell[6] found that the 1 : 1 caesium-zinc salts, if they exist at all, are too soluble to be crystallized in a satisfactory condition, although corresponding ammonium and potassium salts are known.

Professor Remsen[7] called attention to the fact that certain double halides show gradations in water of crystallization, increasing with the atomic weight of the halogen and decreasing with the atomic weight of the alkali metal. An inspection of the list of salts shows that there are many instances of analogous salts to which these rules apply, particularly in the larger amounts of water in sodium and lithium salts and in iodides, and the smaller amounts of water in caesium salts and in fluorides; but, taking the list as a whole, these gradations are not very striking, and there are a few apparent exceptions to them.

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[1] Am. J. Sci., (3), **46**, 432.

[2] *Ibid.*, (3), **46**, 434.

[3] *Ibid.*, (3), **46**, 223.

[4] *Ibid.*, (3), **46**, 432.

[5] Ber. d. chem. Ges., **9**, 1365.

[6] Am. J. Sci., (3), **46**, 434.

[7] This JOURNAL, **14**, 88.

It has been noticed in some cases that caesium halides combine with a greater number of negative halide molecules than do other alkaline halides, while at the other end of a series more molecules of a lighter alkaline halide than of a caesium halide may combine with a negative halide. For instance, the caesium-zirconium and potassium-zirconium fluorides[1] show this relation in the following ratios of their salts:

$CsF : ZrF_4$	....	2 : 1	1 : 1	2 : 3
$KF : ZrF_4$	3 : 1	2 : 1	1 : 1	....

This is evidently not a general rule, however, for there is a 1 : 5 ammonium mercuric chloride corresponding to the extreme type of caesium mercuric chlorides, while at the positive end the caesium-lead and caesium-mercuric salts extend farther than the salts of other alkali metals.

Many irregularities appear in the list. Sometimes fluorides, chlorides, bromides, and iodides seem to be analogous, but often they are not. There are some curious relations of this sort. For instance, all the double fluorides of tellurium are 1 : 1 salts while the other tellurium salts belong to the 2 : 1 type; there is only one chloride among twelve 1 : 1 thallic salts, while all the 2 : 1 salts and nearly all the 3 : 1 salts are chlorides.

Perhaps the most marked case of uniformity in double halides is the invariability of the 2 : 1 type in the salts of the quadrivalent platinum group metals, and this type predominates to a remarkable extent among the salts of the other quadrivalent elements. There are several other well marked groups, such as the 1 : 1 magnesium salts with 6 molecules of water, the 2 : 1 chromium and ferric salts with one water, and the 3 : 2 anhydrous arsenious, antimonious, and bismuth salts.

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[1] Wells and Foote: Am. J. Sci., (4), 1, 18.

It may be stated that in our study of double halides about one-third of the compounds given in the list have been prepared in this laboratory. Some indications of regularity have been observed in connection with these researches, but it must be admitted that the results have been negative as far as throwing light upon the structure of this class of compounds is concerned.

Summary.

In the present discussion, by the method of comparison, the most important conclusion appears to be that the valency of negative halides has little or no influence upon the types of double halides that they form.

It has been shown also that the combining power of negative halides, whatever their valency may be, is nearly the same as that of alkaline halides.

Attention has been called to the prominence of simple types among these double salts.

It has been pointed out that double halides probably increase in ease of formation and variety from the iodides to the fluorides ; but that other gradations and analogies which exist in some cases are probably not general.

The classification of double halides into three groups based upon their behavior in solution has been advocated. (1) Salts that form complex ions. (2) Other salts that can be recrystallized from water or dilute acids. (3) Salts that require the presence of an excess of one of their components for their formation.

New Haven, Conn., May, 1901.

LXXXVIII.—ON SOME ACETYL AND BENZOYL-PSEUDOTHIOUREAS.

By Henry L. Wheeler and Treat B. Johnson.

In a previous paper it was shown that the acylimidomonothiocarbonic esters,

$$RCON{=}C(OCH_3)SCH_3,$$

react with amines[1] as readily as with ammonia.[2] In these reactions the mercapto group is removed and acylpseudoureas are formed,

$$RCON{=}C(OCH_3)NHR.$$

The fact was also established that the phenylimidomonothiocarbonic esters, $C_6H_5N = C(OCH_3)SCH_3$, and the hydrazone of thiocarbonic ethyl ester,

$$C_6H_5NH{-}N{=}C(OC_2H_5)SC_2H_5,$$

do not react in an analogous manner. Indeed these imido esters show a noteworthy inertness when treated with organic bases.[3]

Experiments with the acylimidodithiocarbonic esters,[4]

$$RCON{=}C(SCH_3)_2,$$

have now shown that these compounds give acylpseudothioureas. The action takes place in the cold, and more smoothly than in the case of the corresponding monothioesters,

$$C_6H_5CON{=}C(SCH_3)_2 + HNRR' = C_6H_5CON{=}C(SCH_3)NRR' + HSCH_3.$$

This adds another series to the known types of acyclic pseudothioureas. The simple derivatives of the structure

$$HN{=}C(SR)NH_2.HX$$

were investigated by Claus,[5] Bernthsen and Klinger;[6] the mononitrogen-substituted compounds by Werner[7] and Bertram;[8] while the disubstituted derivaties have been studied by Will, Rathke, Bielschowsky, Reimarus, Evers, Förster, and Noah.[9]

The nearest analogue to our compounds is the monacetylthiolethylisodiphenylthiourea,

$$C_6H_5N{=}C(SC_2H_5)N(C_6H_5)COCH_3,$$

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[1] This JOURNAL, **24**, 189 (1900).

[2] Dixon: J. Chem. Soc. (London), **75**, 378 (1899).

[3] This JOURNAL, **24**, 60, 423 (1900).

[4] *Ibid.*, **26**, 185 (1901).

[5] Ber. d. chem. Ges., **7**, 236 (1874); *Ibid.*, **8**, 41; Ann. Chem. (Liebig), **179**, 145 (1875).

[6] Ber. d. chem. Ges., **11**, 492 (1878); **12**, 575.

[7] J. Chem. Soc. (London), **57**, 283 (1890).

[8] Ber. d. chem. Ges., **25**, 48 (1892).

[9] *Ibid.*, **14**, 1485, 1774 (1881); **15**, 338, 1309 (1882); **19**, 2348 (1886); **21**, 967, 1857 (1888); **23**, 2195 (1890).

of Dains,[1] and this is the only acylpseudothiourea which has hitherto been obtained. This was prepared by the action of acetyl chloride on ethyldiphenylpseudothiourea ; but while it is described as an uncrystallizable oil, most of our compounds, on the other hand, are remarkable for their great tendency to crystallize and for the ease with which they can be purified.

Since the acylpseudothioureas have the structure of amides, amidines, and thioimidoesters combined, it seemed that some of the various cases of structural and stereochemical isomerism, theoretically possible for these compounds, might be met with in this new series. We have therefore prepared benzoylthiolbenzylphenylpseudothiourea,

$$C_6H_5CON{=}C(SCH_2C_6H_5)NHC_6H_5,$$

by the following four methods :

I. The action of aniline on benzoylimidodithiobenzyl carbonate.

II. The action of benzoic anhydride on phenylpseudobenzylthiourea.

III. The action of benzyl chloride on an aqueous sodiumhydrate solution of benzoylphenylthiourea.

IV. The action of benzyl chloride, benzoylphenylthiourea and alcoholic sodium ethylate.

Each of these methods gave one and the same compound, and no evidence was observed of the formation of isomeric products.

The acylpseudothioureas appear to have no basic properties. They do not combine with picric acid. Those which contain a —NH— group are soluble in alkali. Those derived from secondary amines can be distilled at reduced pressure unaltered, while those prepared from primary amines decompose on heating with the formation of mercaptan, substituted acid amides, and other products. A smooth decomposition into carbodiimide derivatives was not observed.

When treated with hydrochloric acid they do not give normal acylureas, as in the case of the oxygen analogues, but decompose or undergo hydrolysis as follows :

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[1] J. Am. Chem. Soc., **22**, 197 (1900).

$$C_6H_5CON{=}C(SC_2H_5)NHC_6H_5 + H_2O + HCl = C_6H_5CONHCO.SC_2H_5 + C_6H_5NH_2HCl.$$

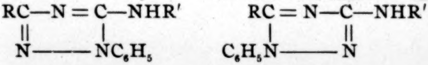
When treated with alcoholic ammonia guanidine derivatives are formed :

$$C_6H_5CON{=}C(SC_2H_5)NHC_6H_5 \rightarrow C_6H_5CON{=}C(NH_2)NHC_6H_5.$$

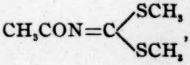
This affords new proof that both of the alkyl groups in the acylimidodithiocarbonic esters are attached to sulphur.

Guanidine derivatives were not obtained by the action of aniline. When the esters were heated with this base they underwent decomposition and benzanilide was obtained.

The acylpseudothioureas readily react with phenylhydrazine to form aminotriazoles. Which of the two following formulas represents the structure of these products will be decided later :



EXPERIMENTAL PART.

Dimethyl Acetylimidodithiocarbonate,[1]  $CH_3CON{=}C(SCH_3)_2$, *and Alcoholic Ammonia*.—Five grams of the ester were allowed to stand for several days with an excess of the ammonia solution. On evaporating the alcohol, an oil was obtained which showed no signs of solidifying on standing. That this consisted mostly of guanidine was shown by mixing with an alcoholic solution of picric acid, whereupon an immediate precipitate of guanidine picrate[2] resulted. Nitrogen determinations gave :

	Calculated for $C_7H_8O_7N_6$.	Found. I.	Found. II.
N	29.16	29.14	29.04

Acetyldiisobutylthiolmethylpseudothiourea, $CH_3CON{=}C(SCH_3)N(C_4H_9)_2$.—Dimethyl acetylimidodithiocarbonate and diisobutylamine reacted at ordinary temperatures. The product was a yellow oil which distilled under 22 mm. pressure at 175° to 177°. A middle portion of this gave, on analysis, the following result :

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[1] Wheeler and Johnson : This JOURNAL, *Loc. cit.*

[2] Emich : Monatsh. Chem., **12**, 23 (1891).

	Calculated for $C_{12}H_{24}ON_2S$.	Found.
N	11.47	11.80

Acetylphenylthiolmethylpseudothiourea, $CH_3CON{=}C(SCH_3)NHC_6H_5$. — When aniline was mixed with dimethylacetylimidodithiocarbonate, mercaptan was evolved in the cold, and, after twelve hours, the material completely solidified. This pseudothiourea crystallized from dilute alcohol in beautiful, long, colorless needles, and melted at 82° to 83°. A nitrogen determination gave :

	Calculated for $C_{10}H_{12}ON_2S$.	Found.
N	13.46	13.31

Benzoylparatolylthiolmethylpseudothiourea, $C_6H_5CO.N{=}C(SCH_3)NHC_6H_4CH_3$.—Dimethyl benzoylimidodithiocarbonate and *p*-toluidine were warmed on the steam-bath until mercaptan ceased to be evolved. On cooling, a solid mass was obtained which crystallized from alcohol in beautiful prisms and melted at 130°. A nitrogen determination gave :

	Calculated for $C_{16}H_{16}ON_2S$.	Found.
N	9.85	9.83

Benzoyl-α-naphthylthiolmethylpseudothiourea, $C_6H_5CON{=}C(SCH_3)NHC_{10}H_7$. — Dimethyl benzoylimidodithiocarbonate and α-naphthylamine gave a product which crystallized from alcohol in balls of fine needles. These melted at 124° and a nitrogen determination gave :

	Calculated for $C_{19}H_{16}ON_2S$.	Found.
N	8.75	8.44

Benzoylmetanitrophenylthiolmethylpseudothiourea, $C_6H_5CON{=}C(SCH_3)NHC_6H_4NO_2$.—Dimethyl benzoylimidodithiocarbonate and metanitraniline readily reacted on warming. The product was soluble in hot alcohol and crystallized in needle-like prisms which melted at 71° to 72°. A nitrogen determination gave :

	Calculated for $C_{15}H_{13}O_3N_3S$.	Found.
N	13.44	13.33

Acetyldiethylthiolethylpseudothiourea, $CH_3CON{=}C(SC_2H_5)N(C_2H_5)_2$. — Diethyl acetylimidodithiocarbonate and diethylamine gave a yellow oil which distilled at 162° to 164° at 21 mm. pressure. A nitrogen determination in a middle portion of this gave :

	Calculated for $C_9H_{18}ON_2S$.	Found.
N	13.86	13.72

Acetylmethylphenylthiolethylpseudothiourea, $CH_3CON{=}C(SC_2H_5)N(CH_3)C_6H_5$, from the ethyl dithiocarbonate and methyl aniline, crystallized beautifully, from petroleum ether, in colorless prisms and melted at 66°. A nitrogen determination gave :

	Calculated for $C_{12}H_{16}ON_2S$.	Found.
N	11.86	11.87

Benzoyldiethylthiolethylpseudothiourea, $C_6H_5CON{=}C(SC_2H_5)N(C_2H_5)_2$, formed colorless rectangular prisms, which melted at 70°, when crystallized from petroleum ether. A nitrogen determination gave :

	Calculated for $C_{14}H_{20}ON_2S$.	Found.
N	10.60	10.61

Benzoyldipropylthiolethylpseudothiourea, $C_6H_5CON{=}C(SC_2H_5)N(C_3H_7)_2$, was obtained as a yellow oil, boiling for the most part at 226° to 229° at 17 mm. pressure. A nitrogen determination in a middle sample of this gave :

	Calculated for $C_{16}H_{29}ON_2S$.	Found.
N	9.59	9.84

Benzoyldiisobutylthiolethylpseudothiourea, $C_6H_5CON{=}C(SC_2H_5)N(C_4H_9)_2$, formed an oil which boiled at 234° to 236° at 21 mm. pressure. A nitrogen determination gave :

	Calculated for $C_{18}H_{28}ON_2S$.	Found.
N	8.75	8.65

Benzoylparatolylthiolethylpseudothiourea, $C_6H_6CON{=}C(SC_2H_5)NHC_6H_4CH_3$.—This crystallized from alcohol in needle-like prisms, which melted at 93°. A nitrogen determination gave :

	Calculated for $C_{17}H_{18}ON_2S$.	Found.
N	9.40	9.24

When this pseudothiourea was heated on the steam-bath with phenylhydrazine, until mercaptan ceased to be evolved, a solid product was obtained which crystallized from alcohol in stout prisms and melted at 225° to 226°. A nitrogen determination gave results agreeing with those calculated for diphenylparatolylaminotriazole :

	Calculated for $C_{21}H_{18}N_4$.	Found.
N	17.14	17.01

Benzoylpseudocumylthiolethylpseudothiourea, $C_6H_5CON{=}C(SC_2H_5)NHC_6H_2(CH_3)_3$, crystallized from alcohol in a mass of fine needles. These melted at 83° to 84°, and a nitrogen determination gave :

	Calculated for $C_{19}H_{22}ON_2S$.	Found.
N	8.60	8.84

Benzoylparaanisylthiolethylpseudothiourea, $C_6H_5CON{=}C(SC_2H_5)NHC_6H_4OCH_3$, crystallized from alcohol in fine, needle-like prisms, which melted at 99° to 100°. The nitrogen determination was as follows :

	Calculated for $C_{17}H_{18}O_2N_2S$.	Found.
N	8.91	8.83

Benzoyldiphenylthiolethylpseudothiourea, $C_6H_5CON{=}C(SC_2H_5)N(C_6H_5)_2$, crystallized from a mixture of benzene and petroleum ether in colorless prisms, and melted at 142°. A nitrogen determination gave :

	Calculated for $C_{22}H_{20}ON_2S$.	Found.
N	7.77	7.80

Benzoylphenylthiolpropylpseudothiourea, $C_6H_5CON{=}C(SC_3H_7)NHC_6H_5$, from propyl dithiocarbonate and aniline formed beautiful colorless prisms, from alcohol, melting at 78° to 79°. A nitrogen determination gave :

	Calculated for $C_{17}H_{18}ON_2S$.	Found.
N	9.39	9.51

Benzoylparatolylthiolpropylpseudothiourea, $C_6H_5CON{=}C(SC_3H_7)NHC_6H_4CH_3$, crystallized from alcohol in colorless needles and melted at 81° to 81°.5. A nitrogen determination gave :

	Calculated for $C_{18}H_{20}ON_2S$.	Found.
N	8.97	9.13

Benzoylmetachlorphenylthiolnormalpropylpseudothiourea, $C_6H_5CON{=}C(SC_3H_7)NHC_6H_4Cl$, formed colorless prisms, from alcohol, which melted at 59° to 59°.5, and a nitrogen determination gave :

	Calculated for $C_{17}H_{17}ON_2ClS$.	Found.
N	8.42	8.59

Benzoylphenyleneguanidine, $C_6H_5CO.N{=}C(NH)_2C_6H_4$. — Diethyl benzoylimidodithiocarbonate, orthophenylenediamine hydrochloride, and sodium ethylate were warmed on the steam-bath. On cooling and crystallizing the product from alcohol, minute, colorless prisms separated, which melted at 237°. This material was insoluble in chloroform, benzene, and water. It was free from sulphur, and a nitrogen determination gave :

	Calculated for $C_{14}H_{11}ON_3$.	Found.
N	17.72	17.63

Diphenylene-di(benzoylthiolethylpseudothiourea), $C_6H_5CON{=}C(SC_2H_5)NHC_6H_4.C_6H_4NH(C_2H_5S)C{=}NCOC_6H_5$.—This compound was obtained when diethyl benzoylimidodithiocarbonate was mixed with benzidine in the proportion of either 1 or 2 molecules of the ester to 1 of the amine. It was difficultly soluble in alcohol, chloroform, and benzene; from a mixture of benzene and alcohol colorless needles were obtained which melted at 179° with slight effervescence. A nitrogen determination gave :

	Calculated for $C_{32}H_{30}O_2N_4S_2$.	Found.
N	9.87	9.80

When this dipseudothiourea was warmed on the water-bath with phenylhydrazine, mercaptan was evolved and a residue difficultly soluble in alcohol was obtained. It formed poorly defined crystals from alcohol which did not melt below 265° and a nitrogen determination agreed with the percentage calculated for a ditriazole of the formula

$$(C_6H_5)_2C_2N_3NHC_6H_4.C_6H_4NHC_2N_3(C_6H_5)_2:$$

	Calculated for $C_{40}H_{30}N_8$.	Found.
N	18.00	17.80

Dimethoxydiphenylene-di-(benzoylthiolethylpseudothiourea), $C_6H_5CON=(CSC_2H_5NHC_6H_3OCH_3.C_6H_3OCH_3NH(C_2H_5S)C=NCOC_6H_5$.—Diethyl benzoylimidodithiocarbonate and *o*-dianisidine formed a difficultly soluble compound which crystallized from a mixture of benzene and alcohol in minute, colorless needles. It melted at 170° to 171°, and a nitrogen determination gave :

	Calculated for $C_{34}H_{34}O_4N_4S_2$.	Found.
N	9.12	9.06

Benzoylphenylthiolbenzylpseudothiourea, $C_6H_5CON=C(SCH_2C_6H_5)NHC_6H_5$. — This compound was prepared by the four methods mentioned in the introduction. It crystallized from alcohol in small, colorless prisms, which melted at 116° to 117°, and a nitrogen determination gave:

	Calculated for $C_{21}H_{18}ON_2S$.	Found.
N	8.09	8.09

When this pseudothiourea was warmed with aqueous hydrochloric acid, a compound crystallizing from alcohol in colorless, needle-like prisms, and melting at 141° to 142°, was obtained. A nitrogen determination agreed with the composition calculated for benzoylthiobenzylcarbamate,

$$C_6H_5CONHCO.SCH_2C_6H_5:$$

	Calculated for $C_{15}H_{13}O_2NS$.	Found.
N	5.16	5.16

On dissolving the pseudothiourea (5 grams) in alcoholic ammonia and allowing the solution to stand for nine days and then evaporating, an oil was obtained. When this was treated with alcohol a mass of crystals separated, melting at 70° to 71° (benzyl disulphide). To the alcoholic solution picric acid was added; a precipitate was formed at once, and on crystallizing from alcohol bright-yellow prisms. melting at 186°, were obtained. A nitrogen determination agreed with the composition calculated for benzoylphenylguanidine picrate, $C_6H_5CON{=}C(NH_2)NHC_6H_5.C_6H_2(NO_2)_3OH$:

	Calculated for $C_{20}H_{16}O_8N_6$.	Found.
N	17.94	17.67

This compound was also obtained by the action of alcoholic ammonia on benzoylphenylthiolethylpseudothiourea and then treating the product with picric acid.

Benzoylphenylguanidine, $C_6H_5CON{=}C(NH_2)NHC_6H_5$, was obtained by treating the picrate with an aqueous solution of sodium hydrate. It was soluble in alcohol and benzene, and it crystallized from a mixture of benzene and petroleum ether in minute, light-yellow prisms, which melted at 90° to 91°. A nitrogen determination gave:

	Calculated for $C_{14}H_{13}ON_3$.	Found.
N	17.57	17.55

Benzoylphenylthiolmetaxylylpseudothiourea, $C_6H_5CON{=}C(SCH_2C_6H_4CH_3)NHC_6H_5$, from dimetaxylyl benzoylimidodithiocarbonate and aniline, crystallized in colorless prisms and melted at 110° to 111°. A nitrogen determination gave:

	Calculated for $C_{22}H_{20}ON_2S$.	Found.
N	7.77	7.82

Benzoyl-α-naphthylthiolmetaxylylpseudothiourea, $C_6H_5CON{=}C(SCH_2C_6H_4CH_3)NHC_{10}H_7$, formed colorless, flattened prisms from alcohol, melting at 133°. A nitrogen determination gave :

	Calculated for $C_{26}H_{22}ON_2S$.	Found.
N	6.83	6.84

NEW HAVEN, CONN., May 30, 1901.

LXXXIX.—ON THE MIXED CRYSTALS OF COPPER SULPHATE AND ZINC SULPHATE.

BY H. W. FOOTE.

Two salts of distinct chemical composition may separate from a solution containing a mixture of the two, in homogeneous crystals, containing both of the salts in indefinite proportions. These are known as "mixed crystals." They may be roughly divided into two classes, the first including those in which the salts may mix in all proportions, and the second including those in which one salt is capable of mixing with but a limited amount of the other.

The alums are an example of the first class. Thus, ammonium and potassium alums can form mixed crystals which contain any desired quantity of either constituent.

The mixed crystals of beryllium sulphate and beryllium selenate are an example of the second class. At ordinary temperatures, tetragonal $BeSO_4.4H_2O$ forms mixed crystals with $BeSeO_4.4H_2O$, ranging from pure $BeSO_4.4H_2O$ to the molecular proportion 7.33 $BeSO_4.4H_2O$: $BeSeO_4.4H_2O$; but no larger proportion of $BeSeO_4.4H_2O$ can exist with $BeSO_4.4H_2O$ in stable tetragonal crystals. If more of the former is introduced, the crystal form changes to orthorhombic, and a series of mixed crystals in this form may be prepared, in which the molecular proportion ranges from $4BeSO_4.4H_2O$: $BeSeO_4.4H_2O$ to pure $BeSeO_4.4H_2O$.[1]

[1] Van 't Hoff : "Vorlesungen über Chemie," Vol. I, p. 49.

If mixed crystals are considered as solid solutions, the salts of the first class, which crystallize together in all proportions, may be compared to perfectly miscible liquids like alcohol and water, while salts of the second class, whose isomorphism is limited, resemble partially miscible liquids, like aniline and water.

As van 't Hoff has pointed out, the composition of the mixed crystals of salts which belong to the second class—*i. e.*, which are only partially miscible with each other—and which are formed at the mixing limit,[1] ought to be a function of the temperature.

There may also be cases in which two salts will combine in all proportions to form mixed crystals within a certain range of temperature, like those of the first class named above, while outside of this range each salt can mix with but a limited amount of the other, like those of the second class; just as aniline mixes in all proportions with water at temperatures above 165°, while below that limit it only mixes to a limited extent.

Roozeboom[2] also states that the composition of mixed crystals should change with the temperature.

These theoretical conclusions are supported by a consideration of the phase rule of Gibbs; for it is clear that any mixed salt has reached its stable mixing limit when there are deposited from its solution crystals of another form. Thus, tetragonal $BeSO_4.4H_2O$ will contain a maximum of $BeSeO_4.4H_2O$ when the concentration of the solution from which it crystallizes is such that the solution is also saturated in regard to the orthorhombic mixed crystals of $BeSeO_4.4H_2O$ containing $BeSO_4.4H_2O$; in other words, when the two forms crystallize together. In such a system there are four phases—vapor, solution and the two solid phases; and three components—the two salts and water. It therefore follows that if we change one of the possible variable conditions, the others will be fixed. This may be seen if the phase rule be expressed in the form: $V = C + 2 - P$, where V represents the number of physical conditions which may be varied, C the number of components present, and P the number of phases. Hence, $V = 3 + 2 - 4 = 1$. The variable conditions are temperature, pressure, and the concentration of the solution and each solid phase. If the temperature be changed, it follows that the other variables must change. With fixed temperature, the concentration of each phase and the vapor pressure must be fixed.

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[1] The term "mixing limit" ("Mischungs-grenze") is used in this paper to represent the composition of mixed crystals of one salt with a maximum of another. Thus, tetragonal mixed crystals of beryllium sulphate and beryllium selenate have reached the mixing limit when their composition is 7.33 $BeSO_4.4H_2O : BeSeO_4.4H_2O$.

[2] Ztschr. phys. Chem. **8**, 530.

So far as the writer knows, no systematic experiments have as yet been made to test this proposition directly, which may be stated thus: When two salts crystallize from aqueous solution, depositing mixed crystals of two crystalline forms, the composition of the crystals, at the "mixing limit," will change with the change of temperature.

The object of the present investigation was to test the influence of temperature on the "mixing limit" of copper sulphate and zinc sulphate and, as will appear below, the experiments have proved that, in accord with the theoretical conclusions adduced, the composition of the mixed crystals, at the mixing limit, changes with change of temperature.

It is well known[1] that copper sulphate, when crystallizing from solutions containing zinc sulphate, forms triclinic crystals of $CuSO_4.5H_2O$, containing a few per cent of $ZnSO_4.5H_2O$, as an isomorphous mixture. As the quantity of zinc sulphate is increased in the solution, monoclinic crystals containing $CuSO_4.7H_2O$ and $ZnSO_4.7H_2O$ in isomorphous mixture are formed, and these give place, in the presence of still more zinc sulphate, to orthorhombic crystals of $ZnSO_4.7H_2O$, containing a small amount of $CuSO_4.7H_2O$.

The following method was adopted for the present work:

Solutions of copper sulphate and zinc sulphate, mixed together and very slightly acidified with sulphuric acid, were prepared in such concentrations that they were very slightly supersaturated at the temperature of experiment.

Several hundred cubic centimeters of the mixed solutions were used in each experiment, so that the deposit of a few grams of crystals would not greatly alter the proportions of copper and zinc remaining in solution.

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[1] Retger: Ztschr. phys. Chem., **15**, 573; Stortenbeker: *Ibid.*, **22**, 60.

The solutions were seeded with a mixture of the two kinds of crystals which it was desired to have form together. Thus, if the solution was of such concentration that the orthorhombic and monoclinic heptahydrates were expected, these two forms were added in minute quantities. If the solution contained more copper sulphate, monoclinic and triclinic crystals, mixed and powdered, were introduced. In case the right proportions of copper and zinc sulphates were not present, only one form would crystallize—that which was stable under the conditions. The gradual addition of more copper or zinc solution would finally produce the conditions where both forms would crystallize together. If the crystals thus obtained were large enough to be separated mechanically, which was often the case, this was done and the separated products were analyzed. If it was impracticable to separate the two forms, they were redissolved and the solution was seeded with but one kind of crystal. The product thus obtained was usually pure, or nearly so, and could be separated mechanically from admixture and analyzed. The composition of the crystals appeared to be practically the same whichever method of separating them was adopted.

The experiments were carried out at five different temperatures, 12°, 25°, 35°, 40°, and 45° C. For maintaining a constant temperature of 12° a thermostat was used, which I have previously described.[1] As the work was done in the winter of 1900–1901, when the temperature of the city water supply ranged between 4° and 8° C., it was unnecessary to cool the water with ice before passing it into the thermostat. An Ostwald thermostat was used to maintain a constant temperature in all other cases.

The analytical methods employed were as follows:

Copper was determined by titration with a solution of sodium thiosulphate, standardized from time to time with weighed quantities of pure copper sulphate. The details of the titration are as follows:

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[1] Ztschr. phys. Chem., 33, 749.

The substance to be analyzed, dissolved in water, is mixed with several grams of potassium iodide dissolved in a little water. The iodine thus set free is titrated with a standard solution of sodium thiosulphate in the presence of starch paste until the blue color just disappears. The method gave entire satisfaction.

Water was determined, whenever the crystal form was uncertain, by the loss on heating very gently in a porcelain crucible till the weight was constant.

If desired, copper was determined in the residue from the water determination by dissolving in water and titrating as above described.

Zinc sulphate was always determined by difference.

The solutions from which the mixed crystals deposited were analyzed by evaporating accurately weighed quantities of them to dryness in porcelain crucibles and igniting gently to constant weight. Copper sulphate was then determined by titration, as above described, in the aqueous solution of the ignited residue and the quantity of zinc sulphate was determined by difference.

It will be noticed below that the composition of different crops of crystals obtained under apparently the same conditions varies considerably. The same result has been noticed before,[1] but the variations in successive crops, as well as from different solutions of about the same concentration, are not great enough to affect the general results.

In tabulating the results below, the percentage of the copper sulphate hydrate is given. This is almost identical with the corresponding molecular percentage, as the atomic weights of copper and zinc are nearly the same.

At 40°, the orthorhombic heptahydrate gave place to the hexahydrate, $(CuZn)SO_4.6H_2O$, and at 45° the monoclinic heptahydrate could no longer be obtained. At this temperature the pentahydrate and the hexahydrate were obtained together.

The following results were obtained for the composition of the mixed crystals :

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[1] Mohr : Ztschr. phys. Chem., **27**, 204 ; Stortenbeker : *Ibid.*, **34**, 108.

Table I.—Percentage of Copper Sulphate Hydrate in Mixed Crystals Obtained at Different Temperatures.

Triclinic $(CuZn)SO_4.5H_2O$ crystallizing with monoclinic heptahydrate. Percentage $CuSO_4.5H_2O$.	Monoclinic $(CuZn)SO_4.7H_2O$ crystallizing with pentahydrate. Percentage $CuSO_4.7H_2O$.	Monoclinic $(CuZn)SO_4.7H_2O$ crystallizing with orthorhombic heptahydrate. Percentage $CuSO_4.7H_2O$.	Orthorhombic $(CuZn)SO_4.7H_2O$ crystallizing with monoclinic heptahydrate. Percentage $CuSO_4.7H_2O$.
	T = 12° C.		
87.15	38.71	15.87	3.76
89.49	38.49	16.65	2.76
88.98	38.69	19.74	3.11
86.73			2.73
89.20			
	T = 25° C.		
78.00	27.79	14.51	2.53
76.00	29.33	12.34	2.48
81.15	29.65	13.68	2.58
81.70	27.09		
79.38	28.41		
	T = 35° C.		
68.85	25.33	10.49	1.98
68.62	25.85	11.34	2.68
67.53	25.81	13.39	2.12
	25.35	13.33	1.92
	24.63	12.85	2.33
	T = 40° C.		
		Monoclinic heptahydrate crystallizing with $(CuZn)SO_4.6H_2O$ Percentage $CuSO_4.7H_2O$.	$(CuZn)SO_4.6H_2O$ crystallizing with monoclinic heptahydrate. Percentage $CuSO_4.6H_2O$.
58.66	26.47	14.74	3.92
58.77	23.32	14.70	3.93
	23.76	15.33	3.68
	24.71	14.22	
		15.09	
	T = 45° C.		
Triclinic $(CuZn)SO_4.5H_2O$ crystallizing with hexahydrate. Percentage $CuSO_4.5H_2O$.	Hexahydrate $(CuZn)SO_4.6H_2O$ crystallizing with pentahydrate. Percentage $CuSO_4.6H_2O$.		
52.12	5.99		
50.51	4.46		
47.04	5.90		
45.08			
50.43			

From the analytical results just given the following averages are computed:

Table II.—Average Percentage of Copper Sulphate Hydrate in Mixed Crystals Obtained at Different Temperatures.

T.	Triclinic crystallizing with monoclinic heptahydrate. Percentage $CuSO_4.5H_2O$.	Monoclinic heptahydrate crystallizing with pentahydrate. Percentage $CuSO_4.7H_2O$.	Monoclinic heptahydrate crystallizing with orthorhomic heptahydrate. Percentage $CuSO_4.7H_2O$.	Orthorhombic heptahydrate crystallizing with monoclinic heptahydrate. Percentage $CuSO_4.7H_2O$.
12°	88.31	38.63	17.42	3.09
25°	79.25	28.45	13.51	2.53
35°	68.67	25.39	12.28	2.21
			Crystallizing with $(CuZn)SO_4.6H_2O$.	$(CuZn)SO_4.6H_2O$ crystallizing with monoclinic heptahydrate. Percentage $CuSO_4.6H_2O$.
40°	58.72	24.56	14.82	3.84
	Crystallizing with $(CuZn)SO_4.6H_2O$.			Crystallizing with pentahydrate.
45°	49.04			5.45

The composition of the crystals at the mixing limit for different temperatures is also seen in Fig. I., the temperature being plotted as ordinate and the percentage of copper sulphate hydrate as abscissa.

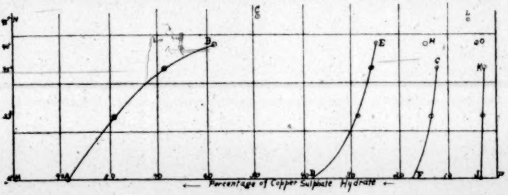

Fig. I.

The line *AB* shows the percentages of copper sulphate hydrate in the mixed pentahydrate salt which forms at the same time with monoclinic heptahydrate.

DE shows the percentages of copper sulphate hydrate in the mixed monoclinic heptahydrate salt which forms at the same time with pentahydrate.

FG shows the percentages of copper sulphate hydrate in the mixed monoclinic heptahydrate salt which forms at the same time with orthorhombic heptahydrate.

JK shows the percentages of copper sulphate hydrate in the mixed orthorhombic heptahydrate salt which forms at the same time with monoclinic heptahydrate.

As is well known, at 39° orthorhombic $ZnSO_4.7H_2O$ passes into $ZnSO_4.6H_2O$, and at 40° mixed crystals of the former could no longer be obtained, the monoclinic heptahydrate forming with the hexahydrate. The points *H* and *O* in the diagram represent the composition of these two forms at 40°. Between 40° and 45° the monoclinic heptahydrate disappears, and at 45° the pentahydrate forms with the hexahydrate. The points *C* and *L* represent the composition of the two forms at 45°. It is evident that a considerable variation in composition has but a slight effect, if any, on the transition temperature of the monoclinic heptahydrate, for while at 40° crystals of this hydrate may be obtained, varying from 24.56 per cent to 14.82 per cent of $CuSO_4.7H_2O$, at 45° it does not form at all.

In the diagram, any point in the area *JKP* represents the percentage of copper sulphate hydrate in stable mixed crystals of the orthorhombic heptahydrate.

Area *DEHGF* represents the percentage of copper sulphate hydrate in the stable mixed crystals of the monoclinic heptahydrate.

Area *NCAM* represents the percentage of copper sulphate hydrate in the stable mixed crystals of the pentahydrate.

It is evident from the results given above and from the diagram that the *composition of the mixed crystals at the mixing limit varies with the temperature.* The variation is, however, not always very great.

It was found impracticable to obtain the mixing limits of the pentahydrate and of the hexahydrate above 45°. The former could only be obtained as a very fine precipitate, and the solutions, which were necessarily very concentrated, dried very rapidly on the crystals when the latter were removed from solution. At both 50° and 55°, however, undoubted crystals of both hydrates were obtained. At 56° $CuSO_4.5H_2O$

passes into a lower hydrate.[1] *It would thus appear impossible that a complete series of stable mixed crystals of* $(CuZn)SO_4.5H_2O$ *can be prepared.*

The composition of the solutions yielding two forms of crystals was found to be as in Table III.

The values given are in molecules of copper sulphate and zinc sulphate to 100 molecules of water are plotted in Fig. II, the temperature as ordinate and the quantity of salt as abscissa.

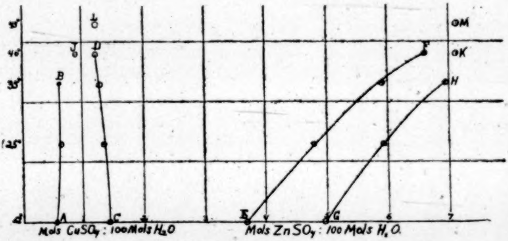

Fig. II.

Curve *AB* = mols. $CuSO_4$: 100 mols. H_2O yielding monoclinic and orthorhombic.

Curve *GH* = mols. $ZnSO_4$: 100 mols. H_2O yielding monoclinic and orthorhombic.

Curve *CD* = mols. $CuSO_4$: 100 mols. H_2O yielding monoclinic and triclinic.

Curve *EF* = mols. $ZnSO_4$: 100 mols. H_2O yielding monoclinic and triclinic.

The points *J* and *K* represent the molecules of $CuSO_4$ and $ZnSO_4$, respectively, to 100 molecules of water, in the solution yielding monoclinic salt and $(CuZn)SO_4.6H_2O$ at 40°. The points *L* and *M*, finally, represent the corresponding values at 45° for the solution yielding triclinic pentahydrate and $(CuZn)SO_4.6H_2O$. As would be expected, these points do not come into the four curves plotted.

It will be noticed in regard to the curves that the amount

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[1] Cohen: Ztschr. phys. Chem., 31, 174.

Table III.—Composition of the Solutions Yielding Two Forms of Crystals.

	Solution yielding triclinic and monoclinic crystals.					Solution yielding monoclinic and orthorhombic crystals.				
	Percentage composition.			Average number of molecules of anhydrous salt to 100 molecules of water.		Percentage composition.			Average number of molecules of anhydrous salt to 100 molecules of water.	
	$CuSO_4$.	$ZnSO_4$.	H_2O.	$CuSO_4$.	$ZnSO_4$.	$CuSO_4$.	$ZnSO_4$.	H_2O.	$CuSO_4$.	$ZnSO_4$.
12°	9.09	22.36	68.55	1.424	3.695	3.50	30.02	66.48	0.570	4.997
	8.23	23.10	68.67			3.24	29.78	66.98		
25°	7.27	28.13	64.60	1.339	4.796	3.33	33.66	63.01	0.641	5.927
	8.03	26.80	65.17			3.84	33.26	62.90		
	7.68	28.38	63.94							
35°	6.26	32.53	61.21	1.297	5.903	3.33	37.04	59.63	0.613	6.947
	7.07	32.19	60.74			3.15	37.24	59.61		
	7.65	31.85	60.50							
						Solution yielding monoclinic and $(CuZn)SO_4.6H_2O$.				
40°	6.46	34.70	58.84	1.237	6.614	4.56	37.36	58.08	0.887	7.113
	6.42	34.97	58.61			4.60	36.96	58.44		
	Solution yielding triclinic and $(CuZn)SO_4.6H_2O$.									
45°	6.38	36.25	57.37	1.227	7.105					
	6.38	36.04	57.58							
	6.25	36.68	57.07							
	5.91	36.99	57.10							

of copper sulphate in both cases remains nearly constant with rising temperature, while the quantity of zinc sulphate increases rapidly and in nearly the same ratio in the two different solutions. The change in the composition of the crystals is not so regular.

Summary.

1. Van't Hoff has pointed out that the composition of mixed crystals at their mixing limit should be a function of the temperature.

2. The same conclusion is reached from a consideration of the application of the phase rule of Gibbs to the matter.

3. The experiments above described demonstrate that this theoretical conclusion reached by van 't Hoff and by the application of the phase rule is correct for mixtures of copper and zinc sulphates, *i. e.*, the composition of stable mixed crystals of copper sulphate and zinc sulphate formed at the mixing limit depends upon and varies with the temperature.

4. That while the composition of the mixed crystals varies with the temperature, the salts named do not form completely isomorphous crystals between 12° and 56° C.

5. That in solutions yielding two forms of crystals, the amount of copper sulphate in solution remains nearly constant with rising temperature, while the amount of zinc sulphate increases very largely with rising temperature.

NEW HAVEN, CONN., June 21, 1901.

THE DISSOCIATION OF CERTAIN ACIDS, BASES, AND SALTS AT DIFFERENT TEMPERATURES.[1]

BY HARRY C. JONES AND JAMES M. DOUGLAS.

Historical Review.

Arrhenius[2] has pointed out the connection between the depression of the freezing-point of a solvent by an electrolyte, and the conductivity of the electrolyte. In most of the earlier experiments, however, the values obtained for the amount of dissociation at zero by the freezing-point method were generally a little lower than those obtained by the conductivity method at 18° or 25°. This would indicate that there is a small temperature coefficient of dissociation.

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[1] From the dissertation of J. M. Douglas, submitted to the Board of University Studies of the Johns Hopkins University for the degree of Doctor of Philosophy, June, 1901.

[2] Ztschr. phys. Chem., 1, 631.

The first piece of work to determine the electrical conductivity at zero was carried out by Wood.[1] He found that the dissociation for very dilute solutions at 0° and 18° is the same. The electrolytes used by him were potassium chloride, sodium chloride, dichloracetic acid, and trichloracetic acid. He did not carry his work far enough to obtain μ_∞, but calculated this by means of temperature coefficients, from the work of Kohlrausch and Ostwald at 18° and 25°. His work was not carried far enough to justify him in drawing any general conclusion.

Whetham[2] carried out a very careful piece of work for the purpose of comparing the ionization values obtained by the conductivity method with the results obtained by the freezing-point method. He used an elaborate piece of apparatus, and tried in every way to minimize the sources of error. He worked with several electrolytes at zero, and compared his values with those obtained at higher temperatures. He thinks that temperature has a slight effect on the amount of dissociation, the higher the temperature the less the dissociation.

E. Krannhals[3] carried out a piece of work with the same dilutions at different temperatures. He worked at temperatures ranging from 18° to 99°.4. He used hydrochloric acid, and several salts which are very good examples of strongly dissociated electrolytes. He calculated the temperature coefficients between 18° and 99°.4. As the dilution increases the temperature coefficient becomes greater. He also concluded that temperature has no effect on the amount of dissociation.

The subject of the influence of temperature on conductivity has been carefully and thoroughly worked out by many experimenters, but through rather narrow ranges of temperature. Grotrian,[1] and Kohlrausch and Grotrian[2] worked out the influence of temperature on conductivity, and also the temperature coefficients for sulphuric and hydrochloric acids, and several other electrolytes. Temperature coefficients for some of the more common salts have been determined by Freund,[3] Long,[4] and Booty.[5] Jahn[6] did a very extensive piece of work on the fatty acids. There is also a dissertation by Carl Deguisne,[7] of Strassburg, in which he has determined the temperature coefficient, in very dilute solutions, for a large number of electrolytes. Arrhenius[8] has done an interesting piece of work along this same line, for temperatures ranging from 18° to 52°.

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[1] Phil. Mag., **41**, 117.

[2] Ztschr. phys. Chem., **33**, 344.

[3] *Ibid.*, **5**, 250.

In all of the above work it was found that conductivity increases with the temperature. Also, that as the dilution increases the temperature coefficients of conductivity become greater. Deguisne concluded from his work that for salts there is an increase in the temperature coefficient with a rise in temperature, while for acids there is a decrease with a rise in temperature.

Introduction.

This piece of work was undertaken for the purpose of determining whether or not temperature has any influence on the dissociation of electrolytes, and, if so, the order of the magnitude of this influence. This work extends over a considerable range of temperatures, *viz.*, from 0° to 35°. We not only determined the percentage of dissociation at the respective temperatures, for the several dilutions of the electrolytes used, but also the temperature coefficient of conductivity for these temperatures.

The electrolytes used were hydrochloric, nitric, and sulphuric acids, potassium hydroxide, potassium chloride, potassium bromide, potassium iodide, potassium nitrate, sodium nitrate, ammonium nitrate, potassium sulphate, and potassium permanganate.

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[1] Pogg. Ann., **151**, 390.

[2] *Ibid.*, **154**, 224.

[3] Wied. Ann., **7**, 47.

[4] *Ibid.*, **11**, 37.

[5] Ann. chim. phys., [6], **3**, 498.

[6] Ztschr. phys. Chem., **16**, 72.

[7] Inaugural Dissertation, Strassburg.

[8] Ztschr. phys. Chem., **4**, 96.

The percentage of dissociation for any dilution of any electrolyte at a given temperature, is the ratio of the molecular conductivity at that dilution to the maximum molecular conductivity of the electrolyte.

Apparatus.

The measurements of conductivity were made by the Kohlrausch method, using the wheatstone bridge, induction coil, and telephone. The Arrhenius type of cells was used. The electrodes were placed at such distances as would give good tone-minima, several cells being used with each substance. Wide electrodes were employed for the more concentrated solutions, and for the more dilute solutions the plates were placed close together. To avoid the error arising from the solubility of the glass at more elevated temperatures, porcelain cups were used for making the measurements at 35°. The temperatures selected were zero, that of the hydrant water which varied from time to time from 7° to 18°, 25°, and 35°. By means of the Ostwald thermoregulator the temperatures of the 25° and 35° baths were kept constant. The baths were kept stirred by fans driven by a gas-jet. The zero bath was prepared as follows : A glass battery jar was filled with pure, well-crushed ice, to which a little redistilled water was added. This was placed in a water-bath, the space between the two being filled with ice and water. The outer bath served to protect the inner bath from the warmer air of the room. The inner bath was stirred from time to time, while the cell containing the solution was immersed in the ice. The temperature was found always to remain within 0°.05 of zero. A constant stream of hydrant water was passed through a large vessel to obtain the temperature intermediate between 0° and 25°. After the stream had flowed for about an hour we found that the temperature remained very constant throughout the day, never varying more than 0°.1 during the time we were making the readings. The temperature would, of course, change considerably from day to day.

Solutions.

The flasks used were carefully calibrated for 20°, by the method devised by Morse and Blalock.[1] The pipettes were also carefully calibrated. The flasks and pipettes agreed with each other. The solutions were prepared at 20°, and generally standardized by analysis. Solutions of some of the salts, however, were made up by weight. Since the purity of the water used would have a marked effect on the results, the orordinary distilled water was redistilled successively from acid and alkaline potassium permanganate, employing a block-tin condenser. The method used was that described by Jones and Mackay.[2]

The conductivity of the water used in making up the solutions was determined, and the corresponding correction applied for each dilution above volume 32.

Conductivity Measurements.

The several dilutions were prepared by taking a measured volume from the original standard solution, and diluting to the desired volume in a measuring flask. To avoid the error resulting from the measurements of very small volumes, only the solutions up to volume 128 were made directly from the original mother-solution. This solution of volume 128 was used as the mother-solution for preparing the more dilute solutions up to volume 2048. Solution of volume 2048, prepared directly from solution of volume 128, was then used as a third mother-solution, and the still more dilute solutions prepared from this as the starting-point. The cell constants were determined very frequently. The constant for any cell used was found to vary but little during the entire year's work. All cells were standardized with a N/50 solution of potassium chloride. In each determination of conductivity, from three to five different resistances were used in the rheostat, the amount of resistance being so chosen that the readings on the bridge were always between 400 mm. and 600 mm.

Each result given is the average of from three to five conductivity measurements. The measurements of the conductivity of the solution were made; the solution was then stirred by quietly raising the electrodes several times. Fifteen or twenty minutes later the conductivity of the solution was again measured. This was a check on the first set of measurements.

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[1] This JOURNAL, **16**, 479.

[2] *Ibid.*, **19**, 83.

For the corrections in volume due to temperatures which were higher and lower than that at which the measuring apparatus was calibrated, we made use of data given by Schulze.[1] The change in volume of dilute solutions was taken to be the same as that of water. Instead of applying the corrections directly to the volume we applied them to the conductivity measurements.

Hydrochloric Acid.

The normal solution of hydrochloric acid was prepared by dissolving pure hydrochloric acid in redistilled water, and titrating against standard solutions of potassium and sodium hydroxides. The hydroxides used were standardized by titrating against sulphuric acid, which had been standardized gravimetrically by precipitation as barium sulphate. The conductivity measurements of Ostwald and Krannhals, at 15°, are given along with our own values for the purpose of comparison. Kohlrausch also determined the conductivity at 18°, but at different volumes. The following measurements were made:

v is the volume of the solution which contains a gram-molecular weight of the electrolyte, and μ_v the molecular conductivity at the temperature in question.

Krannhals' experimental work with hydrochloric acid was done at 18°. The values given in the table were obtained by transforming his values from 18° to 15°. This was done by using the temperature coefficients which we found between 15° and 25°. Krannhals' and Ostwald's values agree very well with our own.

By examining Table III. we see that temperature has practically no effect on the amount of dissociation. The temperature coefficient of conductivity of hydrochloric acid increases as the solution becomes more dilute.

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[1] Ztschr. anal. Chem., 21, 167.

Table I.—Molecular Conductivities of Hydrochloric Acid.

v.	μ_v 0°.	μ_v 15°.	μ_v 15°. (Krannhals.)	μ_v 25°.	μ_v 25°. (Ostwald.)	μ_v 35°.
2	216.5	286.5	287.44	331.7	331.0	371.6
8	228.2	307.2	308.18	356.6	355.0	405.1
16	230.7	310.0	312.68	364.4	362.0	415.2
32	233.6	321.1	319.40	371.1	369.0	420.6
128	239.0	327.5	325.7	378.7	376.0	430.4
256	....	....	327.7	....	378.0	....
512	240.5	327.7		378.7		430.4
1024	240.6	327.7		378.7		430.4
2048	240.4	327.3		378.0		430.4
μ_∞	240.6	327.7		378.7		430.4

Table II.—Temperature Coefficients of Conductivity of Hydrochloric Acid.

v.	0°-15°.	15°-25°.	25°-35°.
2	4.67	4.52	3.99
8	5.27	4.94	4.85
16	5.29	5.44	5.08
32	5.83	5.00	4.95
128	5.90	5.12	5.17
512	5.81	5.10	5.17
1024	5.81	5.10	5.17
2048	5.79	5.07	5.24

Table III.—Dissociation of Hydrochloric Acid at Different Temperatures.

v.	0°.	15°.	25°.	35°.
2	89.9	87.4	87.6	86.3
8	94.8	93.7	94.2	94.1
16	95.9	94.6	96.2	96.5
32	97.1	98.0	98.0	97.7
128	99.3	99.9	100.0	100.0
512	100.0	100.0	100.0	100.0
1024	100.0	100.0	100.0	100.0
2048	100.0	100.0	99.8	100.0

Nitric Acid.

The solution was prepared and standardized in the same manner as the solution of hydrochloric acid—by titrating against standard solutions of potassium and sodium hydroxides. Kohlrausch's measurements for nitric acid were made at 18° and with different volumes, but by transforming his results to 13° and interpolating between his volumes we find that his measurements agree very closely with our own.

Nitric acid, like hydrochloric, is a very strong acid. It is almost completely dissociated at volume 128, and over 87 per cent at volume 2.

As the dilution increases the temperature coefficient also increases. The effect of temperature on dissociation is practically zero.

Table IV.—Molecular Conductivities of Nitric Acid.

v.	$\mu_v\ 0^\circ$.	$\mu_v\ 13^\circ$.	$\mu_v\ 25^\circ$.	$\mu_v\ 35^\circ$.
2	213.3	271.0	323.4	370.4
8	224.4	292.0	350.4	400.5
16	231.4	299.3	360.0	410.5
32	232.0	303.2	365.0	....
128	234.5	306.9	365.4	421.3
512	233.6	306.9	366.3	420.8
1024	235.6	307.0	368.0	421.3
2048	235.6	307.0	368.0	421.3
μ_∞	235.6	307.0	368.0	421.3

Table V.—Temperature Coefficients of Conductivity of Nitric Acid.

v.	0°-13°.	13°-25°.	25°-35°.
2	4.4	4.37	4.70
8	5.22	4.87	5.01
16	5.22	5.06	5.05
32	5.48	5.15	....
128	5.57	4.88	5.59
512	5.64	4.95	5.45
1024	5.49	5.08	5.33
2048	5.49	5.08	5.33

Table VI.—Dissociation of Nitric Acid at Different Temperatures.

v.	0°.	13°.	25°.	35°.
2	90.6	88.3	87.9	87.9
8	95.2	95.1	95.2	95.0
16	98.2	97.5	97.8	97.4
32	98.5	98.8	99.2	....
128	99.5	99.9	99.3	100.0
512	99.2	99.9	99.5	99.9
1024	100.0	100.0	100.0	100.0
2048	100.0	100.0	100.0	100.0

Sulphuric Acid.

The normal solution of sulphuric acid was prepared in the same manner as that of hydrochloric acid and nitric acid. It was titrated against the normal solutions of potassium and sodium hydroxides. The following results were obtained:

Table VII.—Molecular Conductivities of Sulphuric Acid.

v.	μ_v 0°.	μ_v 15°.	μ_v 25°.	μ_v 35°.
2	277.3	346.0	390.0	464.0
8	306.2	391.0	425.9	490.0
16	321.7	410.0	449.8	535.0
32	350.8	445.4	490.0	590.6
128	400.7	508.1	582.8	684.8
512	449.8	571.6	675.0	760.0
1024	475.0	630.0	697.0	842.0
2048	488.3	643.5	705.8	853.0
4096	493.0	650.0	713.0	854.0
8192	495.0	650.0	713.0	856.0
16384	500.0	650.0	713.0	856.0
μ_∞	500.0	650.0	713.0	856.0

Table VIII.—Dissociation of Sulphuric Acid at Different Temperatures.

v.	0°.	15°.	25°.	35°.
2	55.5	53.2	54.7	54.2
8	61.2	60.2	59.7	57.2
16	64.3	63.1	63.1	62.5
32	70.2	68.5	68.7	69.0
128	80.1	78.2	81.7	80.0
512	90.0	87.9	94.7	88.8

v.	0°.	15°.	25°.	35°.
1024	95.0	96.9	97.7	98.4
2048	97.7	99.0	98.9	99.6
4096	98.6	100.0	100.0	99.8
8102	99.0	100.0	100.0	100.0
16384	100.0	100.0	100.0	100.0

We see from the table of molecular conductivities that we do not have complete dissociation with sulphuric acid until a volume of 4096 is reached.

Potassium Hydroxide.

The normal solution of potassium hydroxide by alcohol was prepared by titrating against a standard solution of sulphuric acid. The results obtained by Kohlrausch at 18° are published for the sake of comparison.

From the table of conductivities we see that our values agree very well with those of Kohlrausch at the same temperature. The measurement of the conductivity of potassium hydroxide was at first rather difficult. We then let very strong potassium hydroxide remain in the cells for several days, and then added strong sulphuric and hydrochloric acids. After washing the cells out thoroughly they were standardized, and we experienced no further trouble with the more concentrated solutions. However, for the dilutions above volume 128 the conductivities would change slightly after the solutions had stood several hours, the more dilute the solution the more rapid the change. This change was very much more rapid while the solution was in the cell than while standing in the glass bottles, and was doubtless due in part to the absorption of carbon dioxide from the air. The method pursued for volumes above 128 was to bring the solution to the desired temperature before placing it in the cells. The measurements were then made as quickly as possible. The electrodes were then lifted out of the cell and the temperature of the solution taken. Each of the results given for dilutions above volume 128 are the mean of measurement of six to ten separately prepared solutions. For each solution three or four readings were made, using different resistances. The conductivities of the solutions were always measured immediately after they were prepared, and never after standing two or three hours. Complete dissociation was reached at volume 256. The molecular conductivity of solutions whose dilution was greater than 700 always decreased slightly with increase in dilution.

The same fact is brought out in Kohlrausch's results. Above a volume of 500 there is a slight decrease in conductivity.

The temperature coefficients are less regular for potassium hydroxide than for the acids studied. This is doubtless due to the greater difficulty experienced in making accurate conductivity measurements.

Table IX.—Molecular Conductivities of Potassium Hydroxide.

v.	μ_v 0°.	μ_v 18°.	μ_v 18°. (Kohlrausch.)	μ_v 25°.	μ_v 35°.
1	113.5	171.8	171.8	185.2	214.8
2	118.4	184.1	184.1	197.9	227.9
8	122.8	194.0	(194.9)	201.5	232.2
16	125.3	200.0	202.14	212.0	247.5
32	127.6	205.0	207.55	223.0	256.9
128	133.7	212.4	....	226.0	257.7
256	134.0	214.0	....	226.0	258.0
512	134.0	214.0	....	226.0	258.0
500	....	....	214.0	....	....
μ_∞	134.0	214.0		226.0	258.0

Table X.—Temperature Coefficients of Conductivity of Potassium Hydroxide.

v.	0°-18°.	18°-25°.	25°-35°.
1	3.2	....	2.96
2	3.65	....	3.00
8	3.96	....	3.07
16	4.15	....	3.55
32	4.30	....	3.39
128	4.37	....	3.17
256	4.44	....	3.20
512	4.44	....	3.20

Table XI.—Dissociation of Potassium Hydroxide at Different Temperatures.

v.	0°.	18°.	25°.	35°.
1	84.7	80.3	81.9	83.3
2	88.4	86.0	87.6	88.3
8	91.6	90.7	89.2	90.0
16	93.6	93.5	93.8	95.9
32	95.2	95.8	98.7	99.6
128	99.8	99.3	100.0	100.0
256	100.0	100.0	100.0	100.0
512	100.0	100.0	100.0	100.0

Sodium Hydroxide.

A normal solution of sodium hydroxide was prepared in the same manner as that of potassium hydroxide. Pure samples of sodium hydroxide, by alcohol, were dissolved in redistilled water and titrated against the same standard sulphuric acid that was used for the potassium hydroxide. Kohlrausch's measurements at 18° are also published in the following table:

The same difficulties were encountered in working with sodium hydroxide that were met with in the case of potassium hydroxide. The method pursued for making the conductivity measurements of sodium hydroxide was the same as used with potassium hydroxide. In both cases difficulty was encountered especially in the more dilute solutions.

Our measurements agree very well with those obtained by Kohlrausch for the same temperature. At about volume 200 there is complete dissociation. Kohlrausch found that after volume 166.7 was reached the molecular conductivities gradually decreased. We noticed the same phenomenon in the very dilute solutions. The dilutions were made as with the acids. In both of the hydroxides, temperature has little or no effect on the amount of dissociation. The temperature coefficient of conductivity however, increases with the dilution, but only slightly. The coefficients show marked irregularities, which are doubtless due to experimental errors.

Table XII.—Molecular Conductivities of Sodium Hydroxide.

v.	μ_v 0°.	μ_v 18°.	μ_v 18°. (Kohlrausch.)	μ_v 25°.	μ_v 35°.
1	97.5	147.0	149.0	162.5	189.4
2	104.8	163.0	163.0	177.0	206.5
8	115.0	170.0	168.2	195.0	228.7
16	117.0	174.0	173.2	200.2	232.8
32	121.4	180.0	179.4	205.3	234.5
128	124.0	187.0	....	212.0	244.7
256	125.0	188.0	....	212.0	242.0
512	125.0	188.0	....	210.0	240.0
μ_∞	125.0	188.0	188.0	212.0	244.7

Table XIII.—Temperature Coefficients of Conductivity of Sodium Hydroxide.

v.	0°–18°.	18°–25°.	25°–35°.
1	2.78	....	2.69
2	3.23	....	2.95
8	3.06	3.57	3.37
16	3.17	3.71	3.26
32	3.26	3.61	2.92
128	3.50	3.57	3.27
256	3.50	3.43	3.00
512	3.50	3.14	3.00

Table XIV.—Dissociation of Sodium Hydroxide at Different Temperatures.

v.	0°.	18°.	25°.	35°.
1	78.0	78.2	76.6	77.4
2	83.8	86.7	83.5	84.4
8	92.0	90.4	92.0	93.5
16	93.6	92.5	94.4	95.1
32	97.1	95.7	96.8	95.8
128	99.2	99.5	100.0	100.0
256	100.0	100.0	100.0	98.9
512	100.0	100.0	99.1	98.1

Potassium Chloride.

This salt was recrystallized four times from distilled water, then from redistilled water. It was dried by heating for two days at 150°, then placed in a desiccator until used. The solutions were made up by weight. A gram-molecular weight was dissolved in water and diluted to 1 liter. The conductivity of this salt had been measured by several. Ostwald's and Wood's values are published along with our own for the sake of comparison. Several others have worked at 18°, but their values would have to be transformed from 18° to 7°.1 and also interpolated for volume.

Most of the results obtained by Wood and Ostwald are a little lower than our values. Table XVII shows an increase in the temperature coefficient as the dilution increases. It will be seen that the temperature coefficient for the same volume becomes larger in each case as we pass to higher temperatures. Potassium chloride is completely dissociated at a volume of 1024. The amount of dissociation is practically independent of temperature.

Table XV.—Molecular Conductivities of Potassium Chloride.

v.	μ_v 0°.	μ_v 0°. (Wood.[1])	μ_v 7°.1.	μ_v 25°.	μ_v 25°. (Ostwald.)	μ_v 35°.
1	58.5	61.1	72.4	103.0		121.4
2	62.0	62.49	74.6	108.0		129.0
8	66.7	66.47	76.0	118.7		141.4
16	70.0	68.70	83.8	122.6		147.5
32	72.0	70.66	88.0	128.4	127.3	152.0
128	75.0	73.90	91.0	134.9	133.6	164.3
1024	78.0	76.35	95.0	139.8	139.9	169.0
2048	78.8	....	95.0	139.2	....	169.0
μ_∞	78.8		95.0	139.8		169.0

Table XVI.—Temperature Coefficients of Conductivity of Potassium Chloride.

v.	0°–7°.1.	7°.1–25°.	25°–35°.
1	1.96	1.71	1.84
2	1.78	1.86	2.10
8	1.31	2.38	2.27
16	1.94	2.17	2.49
32	2.25	2.26	2.36
128	2.25	2.45	2.94
1024	2.39	2.50	2.92
2048	2.28	2.47	2.98

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[1] Phil. Mag., 41, 118.

Table XVII.—Dissociation of Potassium Chloride at Different Temperatures.

v.	0°.	7°.1.	25°.	35°.
1	74.2	76.2	73.7	71.8
2	78.7	78.7	78.5	76.3
8	84.6	84.0	80.0	83.7
16	88.8	88.2	88.2	87.3
32	91.4	92.6	92.6	90.0
128	95.1	95.8	95.8	97.2
1024	99.0	100.0	100.0	100.0
2048	100.0	100.0	100.0	100.0

Potassium Bromide.

A comparatively pure sample of potassium bromide was recrystallized three times. The flame test showed no trace of impurity. This salt was then dried by heating in an air-bath for twelve hours, at a temperature of 105°. It was then placed in a desiccator, where it remained until used. The solution was prepared by dissolving 59.555 grams of the salt in water in a liter measuring flask, and diluting to volume.

Krannhals, Ostwald, and Kohlrausch have determined the conductivity of potassium bromide at 18° and 25° for several dilutions. In the few cases in which our volumes and temperatures are the same their results are given with our own.

The measurements at 18° were made at different times and at different temperatures, as can be seen from the table. The measurements were all transformed to 18° by means of the temperature coefficients. Our results agree very well with those of Kohlrausch and Ostwald. Those of Krannhals are, in general, a little lower. There is a gradual increase in the value of the temperature coefficient as the dilution increases. As we pass from 0° to 30° there is a gradual rise in the value of the temperature coefficient, but there is a drop from 30° to 35°. The amount of dissociation remains perfectly constant as the temperature increases from 0° to 35°. For volume 2, temperature 35°, the dissociation found is a little low, but this is in all probability due to experimental error. We are justified in concluing that temperature has little or no effect on the amount of dissociation.

Table XVIII.—Molecular Conductivities of Potassium Bromide.

v.	μ_v 0°.		μ_v 18°.	μ_v 18°. (Krannhals.)	μ_v 25°.	μ_v 25°. (Ostwald.)	μ_v 30°.	μ_v 35°.
2	66.4	98.2(17°.5)	99.2	98.2	113.2		123.1	129.4
8	69.3	105.3(17°.6)	106.1	105.7	120.4		132.6	142.2
16	73.4	109.9(17°.7)	110.1	110.0	125.6		138.9	149.3
32	75.1	......	115.1	113.0	129.0	128.7	141.6	153.2
128	77.5	119.0(17°.8)	120.1	117.0	137.0	136.1	150.2	160.4
512	79.9		123.0		141.0	140.8	158.1	170.6
1024	84.2		125.0		143.4	141.2	160.2	173.2
2048	84.2		125.0		143.4	....	160.2	173.2
μ_∞	84.2		125.0		143.4		160.2	173.2

Table XIX.—Temperature Coefficients of Conductivity of Potassium Bromide.

v.	0°-18°.	18°-25°.	25°-30°.	30°-35°.
2	1.82	2.00	1.98	....
8	2.04	2.04	2.44	....
16	2.04	2.21	2.66	2.08
32	2.22	2.00	2.52	2.32
128	2.37	2.41	2.64	2.04
512	2.40	2.57	3.42	2.50
1024	2.27	2.63	3.36	2.60
2048	2.27	2.63	3.36	2.60

Krannhals found the temperature coefficient between 18° and 99°.4 to be:

v.	18°-99°.4.
1	1.97
16	2.23

Table XX.—Dissociation of Potassium Bromide at Different Temperatures.

v.	0°.	18°.	25°.	30°.	35°.
2	78.8	79.3	78.9	76.8	74.7
8	82.3	84.9	84.0	82.8	82.1
16	87.2	88.1	87.6	86.7	86.2
32	89.2	92.1	90.0	88.4	88.5
128	92.0	96.1	95.5	93.8	92.6
512	94.9	98.4	98.3	98.7	98.5
1024	100.0	100.0	100.0	100.0	100.0
2048	100.0	100.0	100.0	100.0	100.0

Potassium Iodide.

The pure potassium iodide was dried by allowing it to remain in the desiccator for a long time. The solution was prepared as with potassium bromide and chloride. Kohlrausch and Ostwald have measured the conductivities at 18° and 25°. Kohlrausch did not work at the same volumes which we employed, consequently his values were obtained by interpolation. Ostwald's values for 25° agree very closely with our own, but Kohlrausch's values are in some cases a little higher. We find the same general rule to hold for dissociation and temperature coefficients, as has been observed with the preceding compounds.

Table XXI.—Molecular Conductivities of Potassium Iodide.

v.	μ_v 0°.	μ_v 18°. (Kohlrausch.)	μ_v 18°.	μ_v 25°.	μ_v 25°. (Ostwald.)	μ_v 35°.
1	59.8	96.8	94.0	108.1		126.6
2	62.4	99.7	98.8	111.5		132.0
8	66.3	105.1	104.0	120.1		142.3
16	70.6	108.8	107.2	122.9		146.8
32	72.9	112.0	113.7	128.9	128.5	155.0
128	76.4		116.3	135.0	135.4	159.6
512	78.0		119.0	140.0	139.6	166.0
1024	78.0		120.8	141.0	140.7	166.0
2048	78.0		121.0	141.0	....	166.7
μ_∞	78.0		121.0	141.0		166.7

Table XXII.—Temperature Coefficients of Conductivity of Potassium Iodide.

v.	0°–18°.	18°–25°.	25°–35°.
1	1.90	2.01	1.85
2	2.07	1.81	2.05
8	2.16	2.30	2.22
16	2.12	2.24	2.39
32	2.17	2.17	2.61
128	2.11	2.67	2.46
512	2.28	3.00	2.60
1024	2.38	2.88	2.50
2048	2.39	2.86	2.57

Table XXIII.—Dissociation of Potassium Iodide at Different Temperatures.

v.	0°.	18°.	25°.	35°.
1	76.7	77.7	76.7	76.0
2	80.0	81.7	79.1	79.2
8	85.0	85.9	85.2	85.4
16	90.5	88.6	87.2	88.1
32	93.5	94.0	91.4	93.0
128	97.9	96.1	95.9	95.4
512	100.0	98.3	99.3	99.6
1024	100.0	99.9	100.0	99.6
2048	100.0	100.0	100.0	100.0

Potassium Nitrate.

The potassium nitrate used was the product of the fourth fractional crystallization of a very good sample of the salt.

The flame test showed no sodium. The nitrate was dried in an air-bath by heating to 120° for two days. It was then left in a desiccator for three days. A normal solution was prepared by weight. The conductivity of this salt has been determined by Kohlrausch at 18°, Ostwald at 25°, and Krannhals at from 18° to 99°.4.

By transforming their values from 18° to 7° they agree very well with our values. Ostwald's values are given :

Table XXIV.—Molecular Conductivities of Potassium Nitrate.

v.	μ_v 0°.	μ_v 7°.5.	μ_v 25°.	μ_v 25°. (Ostwald.)	μ_v 35°.
1	50.8	61.5	85.0		100.1
2	53.2	....	95.0		113.4
8	60.1	75.0	107.0		128.3
16	65.0	81.2	116.3		140.1
32	70.3	82.8	118.0	120.1	144.0
128	71.6	86.7	128.0	128.0	155.2
512	72.0	93.0	131.0	132.9	157.5
1024	73.6	93.0	130.8	133.0	157.4
2048	73.6	93.0	131.0		158.0
μ_∞	73.6	93.0	131.0		158.0

Table XXV.—Temperature Coefficients of Conductivity of Potassium Nitrate.

v.	0°-7°.5.	7°.5-25°.	25°-35°.
1	1.43	1.34	1.51
2	....	....	1.84
8	1.99	1.83	2.13
16	2.02	2.00	2.38
32	....	2.01	2.60
128	2.01	2.36	2.72
512	2.80	2.17	2.65
1024	2.59	2.16	2.66
2048	2.59	2.17	2.70

Table XXVI.—Dissociation of Potassium Nitrate at Different Temperatures.

v.	0°.	7°.5.	25°.	35°.
1	69.0	66.1	64.9	63.4
2	72.3	....	72.5	71.8
8	81.7	80.6	81.7	81.2
16	88.3	87.3	88.8	88.6

v.	0°.	7°.5.	25°.	35°.
32	95.5	89.0	90.0	91.1
128	97.3	93.2	97.7	98.1
512	97.7	100.0	100.0	99.7
1024	100.0	100.0	99.9	99.6
2048	100.0	100.0	100.0	100.0

The molecular conductivity at 25° agrees fairly well with Ostwald's values. His value for volume 1024 is a little higher than the value which we obtained. We took Krannhals' values for 50° and transformed them to 35°, and found them to agree very closely with our own. The temperature coefficient for potassium nitrate, like the temperature coefficient of the substances thus far studied, increases with increase in dilution. We also notice an increase in the temperature coefficient as we pass from 0° to 35°. The dissociation of potassium nitrate is independent of temperature. The same volumes give practically the same dissociation at different temperatures, except in one or two cases, which seem to be due to some experimental error.

Sodium Nitrate.

The salt was purified by recrystallization. The flame test showed no trace of potassium. It was dried by heating in an air-bath for two days at 120°, and kept in a desiccator until used. The solution was prepared from the pure, dry salt by dissolving a gram-molecular weight in water and diluting to 1 liter. The conductivities of sodium nitrate, as obtained by Krannhals and Ostwald, are also given in the following table.

Krannhals' values were transformed from 18° to 13°. This was done by means of the temperature coefficients found. His results are almost exactly the same as our own. Our values for 25° also agree very closely with those of Ostwald. We notice in sodium nitrate, as in the compounds thus far dealt with, an increase in the temperature coefficients with an increase in dilution. We also notice an increase in the temperature coefficient as we pass from 0° to 35°. Temperature has little or no influence on dissociation.

Table XXVII.—Molecular Conductivities of Sodium Nitrate.

v.	μ_v 0°.	μ_v 13°. (Krannhals.)	μ_v 13°.	μ_v 25°.	μ_v 25°. (Ostwald).	μ_v 35°.
1	40.3	55.1	55.9	70.4		83.8
2	44.9	62.7	62.9	78.7		94.6
8	50.5	71.3	71.0	91.0		108.8
16	53.6	75.5	75.0	97.4		116.5
32	58.2	78.7	79.0	101.7	101.5	122.3
128	61.8	82.1	85.0	108.6	107.6	130.2
512	63.6		87.0	111.5	112.0	135.8
1024	64.0		90.5	113.7	112.7	137.4
2048	64.7		90.9	113.7		138.0
μ_∞	64.7	90.0	90.9	113.7		138.0

Table XXVIII.—Temperature Coefficients of Conductivity of Sodium Nitrate.

v.	0°-13°.	13°-25°.	25°-35°.
1	1.20	1.21	1.34
2	1.36	1.34	1.59
8	1.58	1.67	1.78
16	1.65	1.87	1.91
32	1.58	1.89	2.06
128	1.78	1.97	2.16
512	1.80	2.04	2.43
1024	2.04	1.93	2.37
2048	2.01	1.90	2.43

Table XXIX.—Dissociation of Sodium Nitrate at Different Temperatures.

v.	0°.	13°.	25°.	35°.
1	62.3	61.5	61.9	60.7
2	69.4	69.2	69.2	68.5
8	78.0	78.1	80.0	78.8
16	82.8	82.5	85.7	84.4
32	89.9	86.9	89.4	88.6
128	95.5	93.5	95.5	94.3
512	98.3	95.7	98.1	98.4
1024	98.9	99.6	100.0	99.6
2048	100.0	100.0	100.0	100.0

Ammonium Nitrate.

The salt was recrystallized several times. It was dried in an air-bath and then allowed to remain in a desiccator until used. The solution was prepared by weighing 80.12 grams of the salt, dissolving it in pure water in a liter flask, and diluting to the mark. The conductivity for ammonium nitrate was determined by Kohlrausch for very concentrated solutions at 18°.

Caldwell[1] determined, in this laboratory, the conductivity of ammonium nitrate at 25°.

Table XXX.—Molecular Conductivities of Ammonium Nitrate.

v.	μ_v 0°.	μ_v 9°.	μ_v 25°.	μ_v 35°.
1	55.3	67.4	93.9	111.7
2	58.3	73.2	101.0	....
4	61.2	77.7	107.0	127.8
10	64.3	82.7	114.5	137.2
20	68.1	86.8	119.6	142.9
40	69.6	88.3	123.5	148.4
100	70.2	90.0	126.8	152.2
200	73.7	93.2	129.9	155.3
400	71.3	94.9	131.7	164.1
1000	76.8	100.7	137.2	173.6
2000	78.0	99.0	137.8	170.8
μ_∞	78.0	100.7	137.8	173.6

Table XXXI.—Temperature Coefficients of Conductivity of Ammonium Nitrate.

v.	0°–9°.	9°–25°.	25°–35°.
1	1.34	1.66	1.78
2	1.66	1.75	....
4	1.83	1.83	2.08
10	2.04	1.99	2.27
20	2.08	2.05	2.33
40	2.08	2.20	2.47
100	2.20	2.30	2.54
200	2.17	2.29	2.54
400	2.62	2.30	3.24
1000	2.66	2.28	3.64
2000	2.33	2.42	3.30

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[1] This JOURNAL, 25, 349.

Table XXXII.—Ammonium Nitrate, Dissociation at Different Temperatures.

v.	0°.	9°.	25°.	35°.
1	70.9	66.9	68.1	64.4
2	74.8	72.7	73.3	....
4	78.1	77.2	77.7	73.6
10	82.0	82.1	83.1	89.0
20	87.3	86.2	86.8	82.3
40	89.3	87.7	89.6	85.5
100	90.0	89.4	92.0	87.7
200	94.5	92.6	94.3	89.5
400	91.4	94.2	95.6	94.5
1000	98.4	100.0	99.6	100.0
2000	100.0	98.3	100.0	98.4

We have in this case, as in the other cases, a gradual increase in the temperature coefficient as the dilution is increased. The temperature coefficient in a few cases seems to be a little higher than it should be. This is undoubtedly due to experimental error. The temperature coefficient is a little larger for the higher temperature than for the lower. We notice that in two cases the dissociation is complete at volume 1000, and is a little lower for volume 2000. The percentage of dissociation is very nearly the same at the different temperatures.

Potassium Sulphate.

The potassium sulphate was recrystallized four times. The flame showed no trace of sodium. It was heated for two days in an air-bath at 150° and allowed to remain in a desiccator until used. The solution was prepared by dissolving one-half of a gram-molecular weight of potassium sulphate in a liter flask and diluting to the mark. This solution had a volume of two.

Table XXXIII.—Molecular Conductivities of Potassium Sulphate.

v.	μ_v 0°.	μ_v 18°.	μ_v 25°.	μ_v 25°. (Walden.)	μ_v 35°.
2	86.8	133.4	150.7		175.7
8	103.9	160.1	181.7		218.6
16	113.6	174.7	196.2		235.6

v.	μ_v 0°	μ_v 18.	μ_v 25°.	μ_v 25°. (Walden.)	μ_v 35.
32	122.7	183.0	207.1		254.4
128	138.4	210.5	246.4	246.0	294.7
512	148.1	231.9	266.3	265.4	313.3
1024	157.9	243.8	274.4	272.8	326.3
2048	160.2	247.2	276.0	278.6	330.0
4096	160.2	247.2	276.0		330.0
μ_∞	160.2	247.2	276.0		330.0

Table XXXIV.—Temperature Coefficients of Conductivity of Potassium Sulphate.

v.	0°–18°.	18°–25°.	25°–35°.
2	2.58	2.47	2.50
8	3.12	3.09	3.69
16	3.39	3.07	3.93
32	3.35	3.44	3.73
512	4.65	4.91	4.70
1024	4.77	4.37	5.19
2048	4.77	4.11	5.40
4096	4.84	4.11	5.40

Table XXXV.—Dissociation of Potassium Sulphate at Different Temperatures.

v.	0°.	18°.	25°.	35°.
2	54.2	53.9	54.6	53.2
8	64.8	64.7	65.8	66.2
16	70.9	70.6	71.1	71.4
32	76.6	74.0	75.0	77.1
128	86.3	85.2	89.3	89.3
512	92.4	93.8	96.5	94.9
1024	98.5	98.6	99.4	98.9
2048	100.0	100.0	100.0	100.0
4096	100.0	100.0	100.0	100.0

Potassium Permanganate.

The potassium permanganate used was the product of the second fractional crystallization of a comparatively pure sample of the salt. It was dried and standardized by titrating against a standard solution of oxalic acid.

The conductivities of the more concentrated solutions were not measured, since the oxide would separate out on the electrodes.

Table XXXVI.—Molecular Conductivities of Potassium Permanganate.

v.	μ_v 0°.	μ_v 10°.3.	μ_v 25°.	μ_v 35°.
10.9	59.8	79.7	108.0	129.1
21.8	63.6	82.7	111.0	135.7
43.6	66.0	87.0	115.4	138.4
87.2	67.0	87.3	116.9	140.7
218.0	68.2	89.7	121.0	145.3
872.0	68.7	90.0	121.0	146.0
2180.0	68.0	89.0	121.0	144.0
μ_∞	68.7	90.0	121.0	146.0

Table XXXVII.—Temperature Coefficients of Conductivity for Potassium Permanganate.

v.	0°–10°.3.	10°.3–25°.	25°–35°.
10.9	1.93	1.92	2.11
21.8	1.86	1.93	2.47
43.6	2.04	1.93	2.30
87.2	1.97	2.03	2.38
218.0	2.09	2.12	2.43
872.0	2.07	2.11	2.50
2180.0	2.04	2.11	2.30

Table XXXVIII.—Dissociation of Potassium Permanganate at Different Temperatures.

v.	0°.	10°.3.	25°.	35°.
10.9	87.1	88.6	89.2	88.4
21.8	92.6	91.9	91.7	92.9
43.6	96.1	96.6	95.4	94.8
87.2	97.5	97.7	96.6	96.4
218.0	99.3	99.7	100.0	99.5
872.0	100.0	100.0	100.0	100.0
2180.0	99.0	98.9	100.0	98.6

The molecular conductivities for volume 2180 are a little lower at each temperature, except 25°, than the results for volume 872. This salt is not very soluble in water, and yet we have practically complete ionization at volume 218.

Here, again, we find the same phenomena that have appeared in the preceding cases.

Conclusion.

From the results obtained in this investigation we feel justified in concluding that the temperature coefficient of conductivity increases as the volume increases for acids, bases, and salts. For the salts the temperature coefficient increases as the temperature increases, but for the acids and bases there is so little change that we cannot say whether there is any effect or not.

Temperature does not affect, to any appreciable extent, the amount of dissociation, which is the most important result of this investigation.

This confirms the conclusion drawn a number of years ago, by one of us,[1] from a piece of work done by the freezing-point method. Jones determined, through a wide range of dilutions, the amount of dissociation of a number of acids, bases, and salts, and compared his results with those of Kohlrausch obtained by the conductivity method. The general agreement between the two sets of values is unmistakable. Since the one was obtained at a temperature slightly below zero, and the other at 18°, the temperature coefficient of dissociation must have a very small value.

The temperature coefficient of conductivity is, on the other hand, very large, and a positive quantity. Since conductivity is due to the number of ions present and the velocity with which they move, the effect of increase in temperature might be either to increase the number of ions present, or their velocity, or to increase both. But since it is shown that rise in temperature does not increase, appreciably, the number of ions present, it follows that the influence of temperature on conductivity is to affect the velocities with which the ions move.

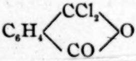
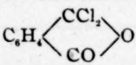
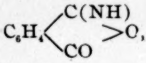
Further work along this line is now in progress in this laboratory.

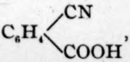
CHEMICAL LABORATORY,
JOHNS HOPKINS UNIV.,
June, 1901.

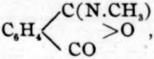
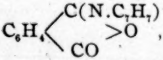
[1] Jones: Ztschr. phys. Chem., **2**, 110, 529; **12**, 623.

ACTION OF AROMATIC AMINES UPON PHTHALYL CHLORIDE AT DIFFERENT TEMPERATURES.

BY M. KUHARA AND M. FUKUI.

Some years ago one of us[1] observed the simultaneous formation of phthalimide and its isomeride by treating phthalyl chloride with aqueous ammonia, and offered a possible explanation of the formation of such an isomeride in these words :[2] "From the knowledge so far gained it seemed as though this substance must be regarded as an isomeride of phthalimide. According to Von Gerichten[3] it appears probable that phthalyl chloride is either  $C_6H_4\left<\begin{matrix}CCl_2\\CO\end{matrix}\right>O$ or a mixture of this substance with the normal chloride. If this view is correct, the formation of a substance isomeric with phthalimide might easily be accounted for. The action of ammonia upon a substance of the formula  $C_6H_4\left<\begin{matrix}CCl_2\\CO\end{matrix}\right>O$ might give rise to a product of the formula  $C_6H_4\left<\begin{matrix}C(NH)\\CO\end{matrix}\right>O$, which would be isomeric with phthalimide."

Afterwards Allendorf[4] obtained the same substance by repeating the process proposed by one of us, but he thinks that it may be *o*-cyanobenzoic acid,  $C_6H_4\left<\begin{matrix}CN\\COOH\end{matrix}\right.$, which was found to change to ordinary phthalimide at a higher temperature.

Auger[5] states that he has obtained unsymmetrical phthalimide from unsymmetrical phthalamide formed from phthalyl chloride by treating with an excess of aqueous ammonia. According to Hoogewerff and Van Dorp's[1] experiments, however, phthalimide and phthalamide have the symmetrical formulas. But they state[2] that they have succeeded in preparing two substituted unsymmetrical phthalimides, namely phthalomethylisoimide,  $C_6H_4<\genfrac{}{}{0pt}{}{C(N.CH_3)}{CO}>O$, and phthalobenzylisoimide,  $C_6H_4<\genfrac{}{}{0pt}{}{C(N.C_7H_7)}{CO}>O$, by treating phthalomethylamic acid and phthalobenzylamic acid with acetyl chloride, respectively.

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[1] This JOURNAL, **3**, 26.

[2] *Ibid.*

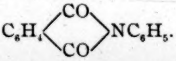
[3] Ber. d. chem. Ges., **13**, 47.

[4] *Ibid.*, **24**, 2348.

[5] Ann. chim. phys., (6), **22**, 289.

Now, in order to determine whether a series of such substances of unsymmetrical imidic nature can really exist, the authors have lately undertaken the study of the action of aromatic amines upon phthalyl chloride at different temperatures.

Action of Aniline upon Phthalyl Chloride.

s-Phenylphthalimide,  $C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>NC_6H_5$. — Ethereal solutions of phthalyl chloride (1 mol.) and aniline (3 mols.) were allowed to act upon each other at ordinary temperature. The precipitate, which is formed immediately after mixing the two substances, was filtered and washed successively with hydrochloric acid, ammonia, and water. The substance thus obtained was purified by repeated recrystallization from alcohol.

It crystallizes in prismatic needles and is insoluble in water, and moderately soluble in hot glacial acetic acid and alcohol. Its melting-point is 203°. This substance is identical with phthalanil prepared by other methods by Laurent and Gerhardt,[3] and also by Doebner,[4] Piutti,[5] and Michael and Palmer.[6] It seems to possess the symmetrical structure as commonly accepted, as will be explained afterwards. We therefore call it *s*-phenylphthalimide.

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[1] Rec. trav. chim., **11**, 84.

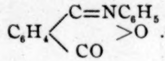
[2] *Ibid.*, **13**, 93.

[3] Jsb. Chem., 1847-48, 605.

[4] Ann. Chem. (Liebig), **210**, 267.

[5] Ber. d. chem. Ges., **16**, 1323.

[6] This JOURNAL, **9**, 202.

a-Phenyl Phthalimide,  $C_6H_4{<}\genfrac{}{}{0pt}{}{C{=}NC_6H_5}{CO}{>}O$.—A moderately dilute ethereal solution of phthalyl chloride, cooled to —10°, was cautiously added drop by drop to an ethereal solution of aniline (3 mols.) cooled to the same temperature. The reaction immediately took place and a white crystalline substance was precipitated after each addition, but it was found to be most advantageous not to allow the temperature of the mixture to rise higher than —5° throughout the course of the experiments. The precipitate, now separated from the liquid by filtration, was thoroughly washed with hydrochloric acid, ammonia, and water, successively, and then repeatedly treated with boiling alcohol to free it from some *s*-phenylphthalimide formed simultaneously and mixed with it. The residue or less soluble portion of the precipitate was dissolved in hot glacial acetic acid and allowed to crystallize. In order to get it in pure state it was found best to recrystallize it from a large quantity of alcohol.

The substance thus prepared consists of groups of white, microscopic, acicular crystals. It is insoluble in water, slightly soluble in alcohol, and readily in hot glacial acetic acid. Its melting-point is 218°, as determined by the capillary-tube method, but 235° as found by Kuhara and Chikashigé's[1] method. The substance dried over sulphuric acid was analyzed and the results are given below:

I. 0.3760 gram substance gave 0.0243 gram nitrogen.
II. 0.2760 gram substance gave 0.0178 gram nitrogen.
III. 0.3950 gram substance gave 0.0254 gram nitrogen.

	Calculated for $C_{14}H_9O_2N$.	Found. I.	II.	III.
N	6.28	6.44	6.45	6.43

From the results of analysis, the substance must be considered to be isomeric with ordinary phenylphthalimide or *s*-phenylphthalimide, and we call this new compound *a*-phenylphthalimide from its unsymmetrical structure, as will be explained afterwards.

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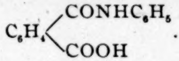
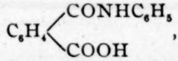
[1] This JOURNAL, 23, 230.

The substance was observed to change to its isomeride or *s*-phenylphthalimide at a high temperature as when it is heated in a sealed tube suspended in *o* xylene at 140°, it passed into solution and again separated out in the form of fine needles which were found to melt at 203° (melting-point of *s*-phenylphthalimide). The substance, perfectly dried over calcium chloride under reduced pressure, was found to change entirely to *s* phenylphthalimide when heated quickly over a flame in a test-tube, but when moist it decomposed partly into aniline and phthalic anhydride. We often noticed the evolution of the characteristic smell of isonitril by simply heating the substance in an oil-bath above 150°.

In order further to examine the action of water upon the substance, it was heated with water in a sealed tube at 140°. After fourteen hours it was found to have changed entirely to *s*-phenylphthalimide, aniline, and phthalic acid. On heating the substance with alcoholic ammonia, part of it decomposed into aniline and ammonium phthalate and a part remained unchanged. This is one of the means of distinguishing *a* phenylphthalimide from *s*-phenylphthalimide, the latter being transformed to ammonium phenylphthalamate, under similar treatment, as shown by Laurent and Gerhardt.[1]

Phenylphthalamic Acid,  $C_6H_4{<}\begin{matrix}CONHC_6H_5\\COOH\end{matrix}$. — The acid usually known as phenylphthalamic acid, the commonly accepted formula of which is  $C_6H_4{<}\begin{matrix}CONHC_6H_5\\COOH\end{matrix}$, was first prepared by Laurent and Gerhardt[2] by boiling phthalanil with alcoholic ammonia. We found, however, that it can readily be formed in the form of the barium salt by boiling *s*-phenylphthalimide with baryta water and removing the excess of baryta by means of carbon dioxide. On concentrating the filtrate the barium salt crystallized out and the crystals dried over sulphuric acid were analyzed.

0 1934 gram substance gave 0.0445 gram barium.

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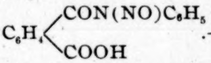
[1] Jsb Chem , 1847-1848, p. 605.

[2] *Ibid.*

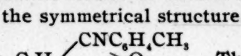
	Calculated for $(C_{14}H_{10}O_3)_2Ba$.	Found.
Ba	22.8	22.8

The free acid can readily be obtained by adding hydrochloric acid to the solution of its barium salt, when it is precipitated in the form of fine crystals. This acid is not formed at all from *a*-phenylphthalimide by similar treatment with either alcoholic ammonia or baryta water.

Oxyphthalylnitrosoaniline,  $C_6H_4\begin{cases}CON(NO)C_6H_5\\COOH\end{cases}$.—Upon 10 grams of phenylphthalamic acid, suspended in 100 cc. of ether, nitrous acid gas was allowed to act. It gradually passed into solution, and after seven hours pale-yellow, fine crystals separated out. They were filtered, well washed with ether, and dried over calcium chloride.

It is easily soluble in water and alcohol and less in ether. It gives Liebermann's nitroso reaction with phenol and sulphuric acid; when heated it explodes, as also by percussion. On boiling with water, it was found to yield chiefly phenol and phthalic acid with evolution of nitrogen, and at the same time some nitrous acid was evolved and some *s*-phenylphthalimide formed. On standing in the air, and even under a desiccator, it gradually decomposes. Owing to the unstable character of the substance, we were not able to analyze it.

Action of Orthotoluidine upon Phthalyl Chloride.

s-Orthotolylphthalimide,  $C_6H_4\begin{cases}CO\\CO\end{cases}NC_6H_4CH_3$.—A number of years ago this compound was prepared by Fröhlich[1] by heating orthotoluidine and phthalic anhydride together; and lately one of us[2] obtained the same substance on heating orthotoluidine and phthalyl chloride together, and already communicated to this JOURNAL the results of studies which support the view that it has the symmetrical structure.

a-Orthotolylphthalimide, $C_6H_4\begin{cases}CNC_6H_4CH_3\\ \quad >O\\CO\end{cases}$.—This new sub-

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[1] Ber. d. chem. Ges., 17, 2679.

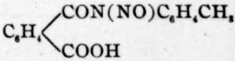
[2] This JOURNAL, 9, 52.

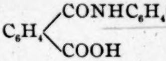
stance was formed from orthotoluidine and phthalyl chloride under conditions similar to those observed at the formation of *a*-phenylphthalimide. It is insoluble in water and readily soluble in hot alcohol. It crystallizes in beautiful silky needles from hot alcohol. Its melting-point is 201°. The crystals, dried over calcium chloride, were analyzed:

I. 0.2530 gram substance gave 0.0134 gram nitrogen.
II. 0.3373 gram substance gave 0.0188 gram nitrogen.
III. 0.4535 gram substance gave 0.0228 gram nitrogen.

	Calculated for $C_{15}H_{11}O_2N$.	Found.		
		I.	II.	III.
N	5.90	5.34	5.57	5.03

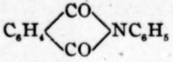
On keeping it in a fused condition for three hours it was found to change to *s*-orthotolylphthalimide with the melting-point 197°. By heating the substance with water in a sealed tube for seven hours, at 120°, it was noticed that a part decomposed to phthalic acid and orthotoluidine and a part changed to *s*-orthotolylphthalimide, but by the action of baryta water it was decomposed almost entirely into orthotoluidine and phthalic acid.

Oxyphthalylnitrosoorthotoluidine,  $C_6H_4<\begin{array}{l}CON(NO)C_6H_4CH_3\\COOH\end{array}$.

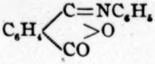
—Orthotolylphthalamic acid,  $C_6H_4<\begin{array}{l}CONHC_6H_4CH_3\\COOH\end{array}$, prepared by boiling *s*-orthotolylphthalamide with concentrated aqueous ammonia, was found to yield a nitroso compound under conditions similar to those of *s*-phenylphthalamic acid by the action of nitrous acid. The behavior of this nitroso compound very much resembles that of the nitroso compound from phenylphthalamic acid in all respects except in its explosiveness, which is not so violent as the former.

Theoretical Views.

Since the existence of two isomeric phthalimides and substituted phthalimides is possible as has been shown in the previous part of the paper, we naturally consider that two isomeric phenylphthalimides are possible, their constitutions being represented by the following formulas:

(*A*) 

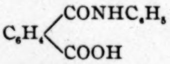
$C_6H_4\left<\begin{array}{l}CO\\CO\end{array}\right>NC_6H_5$

(*B*) 

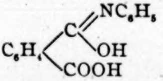
$C_6H_4\left<\begin{array}{l}C{=}NC_6H_5\\ \;\;>O\\CO\end{array}\right.$

But, in fact, we have noticed the existence of two isomeric phenylphthalimides formed by the action of aniline upon phthalyl chloride, one melting at 203° and the other at 235°.

By the action of alkali, *s*-phenylphthalimide ought to yield an acid corresponding to the formula *A′* and *a*-phenylphthalimide, an acid corresponding to *B′* :

(*A′*) 

$C_6H_4\left<\begin{array}{l}CONHC_6H_5\\COOH\end{array}\right.$

(*B′*) 

$C_6H_4\left<\begin{array}{l}C\left<\begin{array}{l}{=}NC_6H_5\\OH\end{array}\right.\\COOH\end{array}\right.$

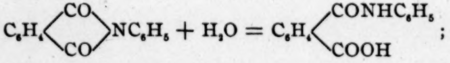
It is highly probable that the acid formed from ordinary phenylphthalimide possesses the structure *A′*, which is in harmony with its formation, transformation, and decomposition :

(1) An acid commonly known as phthalanilic acid (phenylphthalamic acid) is readily formed from ordinary phenylphthalimide by means of baryta water or alcoholic ammonia.

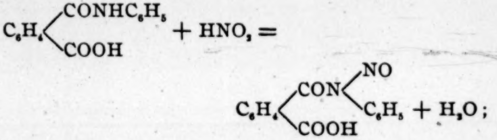
(2) Phenylphthalamic acid yields a nitroso compound by the action of nitrous acid, showing the presence of the imido group.

(3) On boiling the nitroso compound with water, it yields principally phenol and phthalic acid with the evolution of nitrogen, and simultaneously some nitrous acid is evolved with the formation of ordinary phthalimide.

Now, if we admit the correctness of the formula *A* for ordinary phthalimide and *A′* for phthalamic acid, the formation, transformation, and decomposition represented above can readily be interpreted :

(I) 

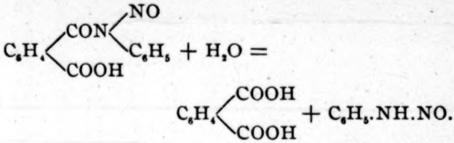
$$C_6H_4\left<\begin{array}{l}CO\\CO\end{array}\right>NC_6H_5 + H_2O = C_6H_4\left<\begin{array}{l}CONHC_6H_5\\COOH\end{array}\right. ;$$

(II) 

$$C_6H_4\left<\begin{array}{l}CONHC_6H_5\\COOH\end{array}\right. + HNO_2 =$$

$$C_6H_4\left<\begin{array}{l}CON\left<\begin{array}{l}NO\\C_6H_5\end{array}\right.\\COOH\end{array}\right. + H_2O ;$$

(III) (*a*)



$$C_6H_4\left\langle\begin{matrix}CON\left\langle\begin{matrix}NO\\C_6H_5\end{matrix}\right.\\COOH\end{matrix}\right. + H_2O = C_6H_4\left\langle\begin{matrix}COOH\\COOH\end{matrix}\right. + C_6H_5.NH.NO.$$

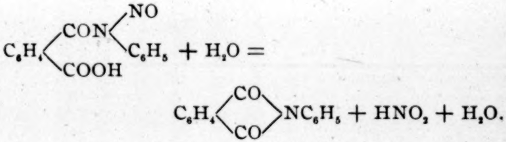
The compound C_6H_5NHNO, which is a desmotropic form of diazobenzene, may soon change to the latter, and the diazobenzene thus formed being incapable of existence immediately decomposes into phenol and nitrogen by the action of water, thus:

(*b*) $C_6H_5.NH.NO \longrightarrow C_6H_5.N:N.OH,$

(*c*) $C_6H_5.N:N.OH = C_6H_5.OH + N_2,$

and the simultaneous formation of nitrous acid and ordinary phenylphthalimide from the nitroso compound may depend upon the following reaction:

(*d*)

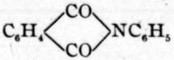


$$C_6H_4\left\langle\begin{matrix}CON\left\langle\begin{matrix}NO\\C_6H_5\end{matrix}\right.\\COOH\end{matrix}\right. + H_2O = C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle NC_6H_5 + HNO_2 + H_2O.$$

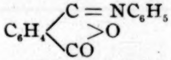
As the ordinary phenylphthalimide appears thus to possess the symmetrical structure, the new and isomeric phenylphthalimide ought to have the unsymmetrical form as described above. And, there are several facts which lend support to the latter view.

The new phenylphthalimide, when perfectly dried, changes with slight decomposition to ordinary phenylphthalimide when heated in a test-tube, but when heated in a sealed tube at 140°, dissolved in an indifferent solvent such as xylene, it undergoes a similar change almost without decomposition, while ordinary phenylphthalimide sublimes without the slightest change even at high temperature. Consequently, phenylphthalimide appears to exist in two forms, a stable and an unstable form.

As ordinary or stable phenylphthalimide has already been found to have the symmetrical structure, it is highly probable that the new or unstable phthalimide possesses the unsymmetrical structure, as the following formulas show:

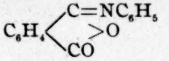


Stable form.
s-Phenylphthalimide.

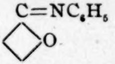


Unstable form.
a-Phenylphthalimide.

On further comparison of the behavior of both phenylphthalimides, that of the new variety points to the unsymmetrical formula as the more probable. On heating ordinary phenylphthalimide with a small quantity of water it undergoes no change at all, while the new phenylphthalimide readily decomposes under this treatment into aniline and phthalic acid, with the simultaneous formation of some ordinary phenylphthalimide. This decomposition of the new phenylphthalimide by water is similar to that of phenyl isocyanate, the latter readily yielding aniline and carbon dioxide under similar conditions. It seems probable, therefore, that the linking of the carbon and nitrogen atoms in both compounds may be alike, as shown in the formulas:

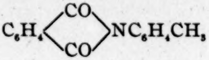


a-Phenylphthalimide.

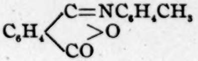


Phenyl isocyanate.

The ordinary and the new orthotolylphthalimides behave exactly like the *s*- and *a*-phenylphthalimides, respectively, as has already been stated. Consequently, ordinary orthotolylphthalimide should possess the symmetrical, and the new one the unsymmetrical structure, as the following formulas show:



s-Orthotolylphthalimide.



a-Orthotolylphthalimide.

It may be that phthalyl chloride exists in two different forms according to the temperature. At ordinary temperature it may assume the normal form and at the lower temperature the unsymmetrical form.

IMPERIAL UNIVERSITY,
KYOTO, April 12, 1901.

REPORT.

The Chemistry of the Purine Group.

In previous numbers of this JOURNAL[1] the important contributions to the chemistry of uric acid and its derivatives have been reported. Within the last few years the subject has been very actively investigated, and as a result this chapter of organic chemistry, which has occupied the attention of Liebig and Wöhler and of A. von Baeyer, has been closed through the magnificent researches of Emil Fischer. These investigations, which have extended over nearly twenty years, have recently been summed up by Fischer[2] in a long article. It is from this source that the following brief review is largely taken.

The older investigators had studied uric acid, xanthine, and hypoxanthine, and had put forward formulæ for these substances expressing the facts which had been established by a study of their reactions; but there was no experimental proof of the relations between them. Fischer speaks with some feeling of the tendency of some chemists to advance complicated formulæ on very insufficient grounds, and calls attention to the fact that too much weight is often given to a successful guess, while a mistake is too readily condoned. Formulæ put forward by Medicus, which have been accepted by chemists, stand as correct only as the result of great labor by Fischer and his helpers.

The discovery by Fischer, about eighteen years ago, of the action of phosphorus pentachloride upon a methyl derivative of uric acid, gave a new point from which to attack these compounds. A substance containing chlorine was formed, which could be converted into a number of compounds by various reagents. This substance had the formula

$$CH_3.C_5N_4Cl_3.$$

It was evidently a substitution-product of a compound of the composition $CH_3.C_5N_4H_3$, which in turn could be considered as a methyl derivative of the complex $C_5N_4H_4$. To a compound of this composition, which was apparently the mothersubstance of the uric acid group, the name purine (from ***purum*** and ***uricum***) was given. The experimental work had, therefore, a new and definite aim—the preparation of purine and its derivatives, and the proof of their structure.

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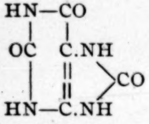
[1] This JOURNAL, 6, 360; also 4, 406 and 12, 138.

[2] Ber. d. chem. Ges., 32, 435.

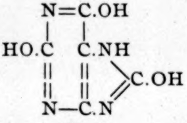
The empirical relations between the simple members of the group are represented as follows :

$C_5N_4H_4$	$C_5N_4H_4O$	$C_5N_4H_4O_2$	$C_5N_4H_4O_3$
Purine.	Hypoxanthine.	Xanthine.	Uric acid.

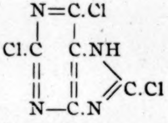
The structure of uric acid is represented by formula I. below—that of Medicus—or by formula II.



I.



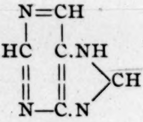
II.



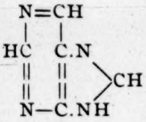
III.

The first is in accord with most of the well established facts; by the use of the second, however, the action of phosphorus pentachloride upon uric acid can be more readily followed. In this action three oxygen and three hydrogen atoms are replaced by three chlorine atoms, and trichlorpurine (formula III.) is formed. The acid contains, therefore, apparently three hydroxyl groups. On account of the fact that it is impossible to distinguish experimentally between the lactam and lactim formulæ, the older formula for uric acid is used. The same kind of tautomerism is observed in the case of the other oxygen derivatives of purine.

Trichlorpurine (formula III.) is converted into purine by replacing the chlorine atoms by hydrogen. The structure of purine is, therefore, represented by formula IV. Methyl derivatives of the tautomeric form (formula V.) have been prepared, but only one hydrogen compound has been isolated.



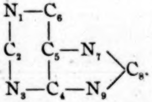
IV.



V.

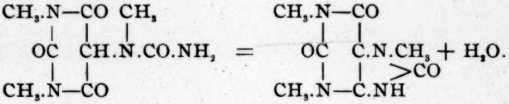
Purine yields mono-, di-, and trioxy, as well as halogen, amino, sulpho, and hydrazo derivatives. From these substances methyl derivatives have been prepared in great number on account of the unusual chances for isomerism.

In order to facilitate naming the compounds the atoms in the purine chain have been numbered in the following manner:



In the preparation of these compounds three general methods have been employed:

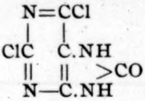
(1) Derivatives of uric acid have been prepared by the condensation of pseudouric acids. This synthesis, which had been used to some extent by the early investigators, was made of great practical value by Fischer by using as dehydrating agent oxalic or hydrochloric acid. Starting with pseudouric acids containing methyl groups in the ring or side chain, a number of isomeric substances have been prepared. In this way hydroxycaffeine was formed from 1,3,7-trimethylpseudouric acid:



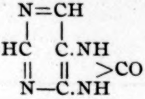
(2) A number of compounds have been prepared by the introduction of alkyl groups into uric acid and other purine derivatives. Fischer improved this method markedly by introducing the groups in the wet way. By working in alkaline solution, many substances were obtained by varying the temperature and the proportions of the reagents. This method furnished the first direct synthesis of caffeine from xanthine.

(3) The preparation of purine derivatives through the chlorpurines is the most important method. These chlorine compounds are prepared by the action of phosphorus oxychloride and pentachloride on the oxygen compounds. By regulating the action of the chlorinating agent the oxygen atoms can be replaced step by step. For example, phosphorus pentachloride at 160° converts the potassium salt of uric acid into 8-oxy-

2,6-dichlorpurine (formula VI.). At a higher temperature



VI.



VII.

three atoms of oxygen are removed by phosphorus oxychloride and trichlorpurine is formed. When 1,3,7-trimethyluric acid is treated in the same way only one chlorine atom is introduced. In some cases phosphorus pentachloride causes the elimination of one or more of the methyl groups; 3,7,9-trimethyluric acid, for instance, is converted by the chloride into 7,9-dimethyl-8-oxy-2,6-dichlorpurine. All of the chlorine compounds can be readily reduced. In this way trioxypurines can be converted into dioxy- and monoxypurines. For example, uric acid (trioxypurine) can be changed into 8-oxy-2,6-dichlorpurine, which, by reduction, becomes a monoxypurine (formulas VI. and VII. above).

Oxyhalogen compounds readily yield to hydriodic acid and phosphonium iodide and give hydrogen derivatives. When no oxygen is present, however, the chlorine substitution-products are completely decomposed by the reducing agents at ordinary temperature; but at 0° they are converted into iodo compounds, which can, in turn, be reduced by means of zinc dust. For example, 7-methyldichlorpurine gives 7-methyliodopurine, which can be converted into 7-methylpurine. If a chlorpurine is treated with zinc dust directly, a part of the halogen is left in the compound. 7-Methyltrichlorpurine is in this way changed into 7-methyl-2-chlorpurine.

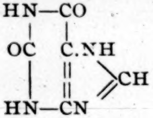
Water, acids, and alkalies react with the chlorpurines and cause a partial or complete conversion of the halogen atoms into hydroxyl groups. Sodium hydroxide, for example, reacts with trichlorpurine at ordinary temperature to form 6-oxydichlorpurine, while at 130°, with hydrochloric acid, uric acid is formed.

An aqueous solution of potassium hydrosulphide converts chlorpurines into thiopurines. With ammonia, aminopurines are formed, which, with nitrous acid, yield oxy-derivatives.

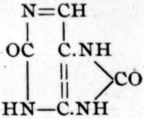
Combinations of the methods briefly outlined above have produced a large number of substances, which exhibit the phenomenon of isomerism in a marked degree. While all the isomers which are possible as a result of the structural formulæ put forward for the simplest members of the purine group have not in every case been prepared, the number definitely established is very large, and each compound has found its place in the system.

Uric acid and its derivatives have been exhaustively studied. It is the only trioxypurine possible. The structure assigned to it calls for a number of methyl derivatives in which the radical is joined to nitrogen. There are 4 monomethyl, 6 dimethyl, 4 trimethyl, and 1 tetramethyl derivatives. The compounds have all been prepared, and the structure has been established in each case.

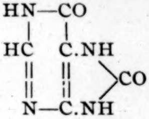
There are three possible dioxypurines which contain the oxygen linked as in uric acid. Their formulæ are as follows:



VIII.



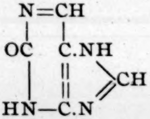
IX.



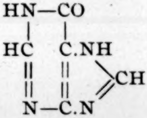
X.

Compounds having the structure of formulæ VIII. and IX. and methyl derivatives of the formula X. are known. 2,6-Dioxypurine, which is xanthine (VIII.), should furnish 3 mono-, 3 di-, and 1 trimethyl derivatives. They have all been prepared. Five methyl derivatives of 6,8-dioxypurine and 2 of 2,8-dioxypurine are also known.

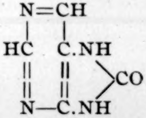
Of the 3 monoxypurines those having formulæ XI. and XII. have been isolated.



XI.



XII.



XIII.

6-Oxypurine (XII.) is the natural product hypoxanthine. It has been prepared synthetically from trichlorpurine. Four of its methyl derivatives and all of those of 8-oxypurine have been described, while but one substance derived from 2-oxypurine is known.

From the above it is seen how complete is the series of oxygen compounds. In addition to these, the purine group contains a large number of amino, thio, and halogen derivatives, as well as substances which contain two or more groups of a different nature. In all 146 purine derivatives have been described, and of this number all but 18 are the result of the work of Fischer and his pupils.

The methods which have been used to determine the structure of the members of this group include both synthesis and the regulated decomposition into simpler known compounds. In many cases both methods have been applied to the same substance with confirmatory results. In order to illustrate the methods, one of the proofs of the structure of 3,7,9-trimethyluric acid will be given.

When uric acid is treated with methyl iodide under certain conditions, a monomethyl derivative is obtained. This compound is readily split into alloxan and methylurea. The methyl group is, accordingly, in the imidazole ring, for uric acids containing a methyl group in the other ring give methyl alloxan. When this methyluric acid is heated with hydrochloric acid it is decomposed into carbon dioxide, ammonia, methylamine, and glycocoll. The formation of the latter substance shows that the methyl group occupied position 9. This 9-methyluric acid is converted by phosphorus pentachloride into a 9-methyloxydichlorpurine. The position of the oxygen and chlorine atoms is immaterial as far as the present line of proof goes. This substance yields a dimethyl compound, which gives sarcosine when heated with hydrochloric acid. As the formation of glycocoll is evidence of the presence of a methyl group in position 9, so the formation of sarcosine indicates that there is a methyl group in position 7. The compound is, therefore, 7,9-dimethyloxydichlorpurine. Water removes the chlorine and a dimethyluric acid results, which must have the substituting groups in positions 7 and 9. This compound yields a trimethyl derivative. As the same substance is obtained by the methylation of 3,7-dimethyluric acid, it is evidently 3,7.9-trimethyluric acid.

A brief account of the synthesis and the determination of the structure of a few important members of the group will further serve to make the methods clear. Xanthine is prepared from uric acid, as follows: The acid is converted, by means of phosphorus pentachloride, into trichlorpurine, which yields, with hydriodic acid, diiodopurine. This compound loses its halogen when heated with hydrochloric acid, and, as a result, xanthine is formed. When the lead salt of xanthine is heated with methyl iodide, two methyl groups are introduced in positions 3 and 7, and theobromine is formed. When methylated in alkaline solution, xanthine gives 1,3,7-trimethylxanthine (caffeine).

Theobromine has been prepared without the intermediate formation of xanthine. Uric acid was converted into its 3-methyl derivative, from which was prepared 3-methylchlorxanthine by means of phosphorus pentachloride. This compound on methylation was converted into 3,7-dimethylchlorxanthine, which was readily reduced to theobromine.

Six independent syntheses of caffeine have been devised. In the one cited above uric acid was the starting-point. In another interesting synthesis dimethylalloxan was converted into 1,3,7-trimethylpseudouric acid, from which xanthine was easily obtained.

The structure of theobromine is proved by effecting its synthesis from 3,7-dimethyluric acid through 3,7-dimethyloxychlorpurine. The structure of caffeine follows from its numerous syntheses, which can be traced, step by step. It is further proved by its decomposition-products. Chlorine in aqueous solution splits it into dimethylalloxan and methylurea. It contains, as a consequence, two methyl groups in the alloxan ring. The third methyl group is shown to occupy position 7 by the formation of sarcosine when caffeine is decomposed by barium hydroxide.

The preparation of purine was effected only toward the end of the work, after a great amount of research. The method of reduction with hydriodic acid and phosphonium iodide, which proved of such great value with a number of chlorpurines, could not be used to convert trichlorpurine into purine. At ordinary temperature the reagents caused the complete decomposition of the compound. It was discovered, finally, that at 0° a partial reduction took place and diiodopurine was formed. The halogen was removed from this substance by zinc dust, and purine was obtained. The compound is a high-melting substance whose great solubility in water is in striking contrast with the small solubility of its derivatives. It is inert toward oxidizing agents and possesses acid and strong basic properties.

The work which has been reviewed is almost entirely that of Fischer. While other chemists have been doing good work in this field of late, they have not added materially to the theoretical side of the subject, and, consequently, their investigations have not received the attention which they would merit in a more extended account of this important chapter of organic chemistry.

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REVIEWS.

SELECT METHODS IN FOOD ANALYSIS. By HENRY LEFFMANN, A.M., M.D. and WILLIAM BEAM, A.M., M.D. pp. 383. Philadelphia: P. Blakiston's Son & Co. 1901. Price $2.50.

The unique value of this book lies in the fact that it gathers together better than has been done anywhere else the methods of food analysis which have appeared in the bulletins of the United States Department of Agriculture and of the Association of Official Agricultural Chemists. Many of these are now out of print and difficult of access and the publication of the more important parts of many of them in a permanent form will prove very useful.

The work is not, of course, confined to material from the source mentioned, but covers the general subject of food analysis in a comprehensive manner. About 70 pages are devoted to general analytical methods, both physical and chemical. Twenty pages are given to the discussion of general methods for the detection of poisonous metals, colors, and preservatives. In the remainder of the book special topics are considered, including starch, flours and meals, sugars, fats and oils, milk and milk products, tea, coffee, cocoa, condiments and spices, alcoholic beverages, meats and meat extracts.

The selection of material is, in general, satisfactory, and as much is included as could be expected of a book of this size. Occasionally there is a tendency to describe complex forms of apparatus which are useful when many determinations of the same kind are to be made, but which are less suitable than simpler forms for the occasional use of most laboratories. For distillation under diminished pressure, for instance, it would be well to give the simple combinations of ordinary apparatus which may be used in any laboratory having water under pressure.

A few slips indicate the haste with which the book has been prepared. Thus, under indicators, the weights of methylorange and of cochineal to be taken in preparing solutions are given but not the volume of the solvent. Such errors are not, however, numerous, nor important. W. A. N.

ELEKTROCHEMISCHES PRAKTIKUM. Von RICHARD LORENZ, Dr. phil., ord. Professor am eidg. Polytechnikum in Zurich, Vorstand der Abtheilung für Elektrochemie und physikalische Chemie. Mit 90 Abbildungen im Text. Göttingen: Vandenhoeck und Ruprecht. 1901. pp. 234.

This excellent little book by Lorenz undoubtedly supplies a need in the field of electrochemistry. There are books which have to do with special phases of electrochemistry, as conductivity, or electrolytic separation of the metals, etc., but there is no work available having the same scope as the one in hand. This will be seen by a glance at its contents. The first part of the work deals chiefly with the apparatus used in making electrochemical measurements.

The second part is especially interesting, dealing with the electrolytic preparation of a number of familiar compounds, such as potassium chlorate, perchlorate, persulphate, permanganate, etc. The purification of a number of substances by electrolysis is also taken up.

Analysis by electrolysis, and electrolytic methods applied to copper, silver, zinc, cadmium, iron, antimony, tin, mercury, lead, etc., are treated of at some length. This chapter is very useful at present, since analysis by electrolysis, as is well known, has come into great prominence in the last few years.

The rest of the book has to do mainly with the measurement of electromotive force.

The book is clearly written and well illustrated, and is a valuable addition to the literature of physical chemistry. As a laboratory guide in electrochemistry, it is sure to find its place in every laboratory where electrochemical work is done.

H. C. J.

JAHRBUCH DER CHEMIE. Bericht über die wichtigsten Fortschritte der reinen und angewandten Chemie. Unter Mitwirkung von H. BECKURTS (Braunschweig), C. A. BISCHOFF (Riga), E. F. DÜRRE (Aachen), J. M. EDER (Wien), P. FRIEDLAENDER (Wien), C. HAEUSSERMANN (Stuttgart), F. W. KÜSTER (Clausthal), J. LEWKOWITSCH (London), M. MÄRCKER (Halle), W. MUTHMANN (München), F. RÖHMANN (Breslau), herausgegeben von RICHARD MEYER (Braunschweig). X Jahrgang, 1900. Braunschweig: Druck und Verlag von Friedrich Vieweg und Sohn. 1901. 555 pp. Price, 14 marks.

Again chemists will experience the pleasure which the editor and publishers of this excellent publication prepare for them annually. Whatever branch of chemistry one may be interested in, this volume will give him a clear, satisfactory résumé of the work done in his special line. The titles of the chapters and the authors are as follows: Physical Chemistry, by F. W. Küster; Inorganic Chemistry, by W. Muthmann; Organic Chemistry, by C. A. Bischoff; Physiological Chemistry, by F. Röhmann; Pharmaceutical Chemistry, by H. Beckurts; Chemistry of Food Stuffs, by H. Beckurts; Agricultural Chemistry, by M. Märcker and by W. Naumann; Metallurgy, by E. F. Dürre and Fr. von Kügelgen; Fuels and Explosives, by C. Haeussermann; Technology of the

Carbohydrates and Brewing, by W. Märcker, W. Naumann, and E. H. Schultze ; Technology of the Fats and Petroleum, by J. Lewkowitsch ; The Chemistry of Tar and Dyes, by Richard Meyer ; Chemical Technology of the Textile Fibers, by P. Friedlaender ; Photography, by J. M. Eder and E. Valenta.

Judging by the previous volumes, this one will prove of great service to all working chemists. It will serve to recall to their minds those investigations which they are already somewhat familiar with through reading of the journals, and will, no doubt, also reveal many interesting articles that are not so familiar. It is a book which should be in every chemical library.